

The Effect of Support on the Heterogeneous Catalysis of Cobalt Complexes

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for the Degree of

Master of Technology

by

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to the

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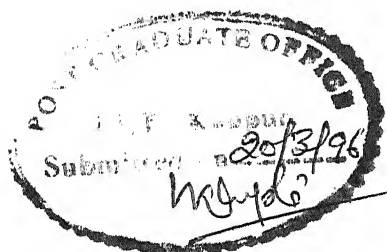
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(Dr. ANIL KUMAR)

18th March. 1996
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DEPARTMENT OF CHEMICAL ENGINEERING
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*Dedicated to the two
Divine and Holy Souls
Whose convergence gave me
an opportunity to explore
This beautiful World.*

MY
PARENTS

Abstract

Two supports for holding the cobalt atom have been prepared for heterogeneous catalysis of the oxidation of saturated hydrocarbons, n-hexane and paraffin wax. The first is a styrene-divinylbenzene copolymer beads on which Salen functional groups were generated using three step synthesis procedure. The catalyst vanadium acetylacetonate and cobalt acetate is chelated on its surface as confirmed by EPMA analysis. The second support studied was silicagel on which the metal was loaded by physical adsorption from the solution of the salt. We have studied the oxidation of n-hexane and paraffin wax in the presence of this catalyst using molecular oxygen and have compared the results obtained from these with that obtained from the oxidation using blank cobalt acetate without any support. It was found that the silicagel supported cobalt catalyst gives the highest conversion of n-hexane having high selectivity towards the formation of alcohols. From this study we infer that the support used for heterogenizing catalytic reagent plays a vital role in the overall kinetics of the chemical reaction.

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Chapter 1

Introduction

Metal salts, complexes and elements having multiple valencies are found to serve as catalysts in a homogeneous medium[1-9]. These homogeneous catalysts are becoming less important because of severe conditions of reaction, contamination of final products and difficulty of catalyst recovery. The advantages gained in heterogenizing the metal complex catalysts are the following.

- The supported solid catalyst can be easily separated from the fluid phase, simply by filtration. This avoids exposing the reaction products to unnecessary solvent extraction, distillation and/or chromatographic separation techniques.
- The spent reagent can be easily recovered and possibly recycled.
- The reactions are faster and can be carried out under comparatively milder conditions.
- The solid supported catalysts are usually nontoxic and environment friendly, and thus solves the burning problem of environmental pollution.

Extensive research has been carried out in the field of heterogeneous catalysis[10-18]. The supporting materials used include sand, diatomaceous earth, glass, activated carbon, kieselguhr, silicagel, zeolites and polymer supports. In heterogenizing the catalysts, the metal salts are, either physically adsorb on the surface or complexed with suitable functional groups present on its surface or inside the pores.

Silicagel is one of the cheapest solid support for heterogenizing the catalyst. Oxidation of hydrocarbons like, alcohols, ketones and aldehydes has been carried out by supporting oxides of chromium on silicagel[19-26], or potassium permanganate adsorbed on silicagel[27-29]. Oxidation of inorganic sulfides like mercaptans to sulfones and sulfoxides has also been carried out using sodium metaperiodate supported on silicagel[30-32]. Cerium salts has also been reported to bring about oxidation of hydroquinones and catechols to quinones[26,33-36]. Chhabra et.al.[37,38], has used selenium dioxide supported on silicagel used for the oxidation of the methyl group of allylic compounds. Oxides of cobalt supported on silicagel[39-42] and other metal complexes like iron, platinum, ruthenium, ruthenium-copper, vanadium, rhodium and palladium supported on silicagel has also been used for the oxidation of n-alkanes, alkenes and alkynes[43-49].

Zeolites have been used as supports for a large number of metal ion complexes. Extensive research has been carried out on the use of these for the oxidation of hydrocarbons[50-64]. Activated carbon, clays and modified clays are also one of the materials for supporting reagents, along with activated charcoal[30,65-67].

Crosslinked polymeric macroreticular or macroporous beads are another class of material used as supports for catalysts. These are polymeric resins with highly crosslinked and porous structure. These materials are modified on the surface with suitable functional groups which complex with metal ions[17,68-79]. Thus prepared catalyst have also been used for separation of metals[70-73], or as super sorbents[80]. Research has also been carried out on the modification of structure of these polymeric beads[81-84] and several novel beads were prepared[85-90]. These modified polymer supported reagents has been used as reagents[70-73,91-94], catalysts[95-99] and phase transfer catalysts[100-111]. For carrying out various organic reactions, their inside pores have a great influence on the final reactivity[112,113]. One of the problems associated with the long term usage of polymer supported catalysts in a continuous fixed bed reactor, is the loss of metal ion complexes. This occurs because the attached metal is involved in dissociation equilibrium under catalytic conditions. The leaching of metal ion complexes can be reduced either by increasing the ligand concentration in polymers or using complexes of the metal which do not leach out during reaction.

In this work we have made an attempt to study the effect of various solid supports used for heterogenizing the catalytic reagents. For this purpose we have used modified polymer

beads as well as silicagel supporting the metal salts by physical adsorption. Experiments show that the later gives higher conversion but the catalytic activity of the metal falls to half its initial value in the reaction due to leaching. The effect of the support was studied on the oxidation of saturated hydrocarbons (n-hexane and paraffin wax in our case). The above prepared catalyst was used for the oxidation of n-hexane and paraffin wax and have conducted the reactions to determine the effect of reaction conditions on the overall conversion of the alkane. Our catalyst was observed to be highly selective towards the formation of alcohols. We have also compared the results obtained, with that obtained from the use of blank cobalt acetate without any support. The oxidation of paraffin wax was also carried out using this catalyst and the products formed was observed to be mainly alcohols. The viscosity of the product for large times was found to decrease suggesting the breakage of long carbon chains. We have determined hydroxyl functional groups and the analysis suggests a high degree of hydroxylation to the extent of three to four -OH groups per chain.

Ref. No.	Catalyst	Reactants	Products	Remarks
19-26	Chromium reagents as oxidant on Silica - Alumina	Primary and secondary alcohols, alkenes and alkynes (-)-menthol	Aldehydes and ketones menthone	Reaction time 5-24 hours and yields of 60-80% Reaction time of 2 hours and yields of 96% yield of 90% and selectivity of 80%
27-29	Potassium permanganate as oxidant on silicagel	alcohols in benzene as diluent benzyl alcohol	aldehydes benzaldehyde	Reaction time of 2 hours at 70°C, yield of 4-55% typical yields are 98% in methylene chloride and 55% in benzene
30-32	Sodium metaperiodate as oxidant on silicagel	hydroquinones in methylene chloride and benzene as solvent	quinones	
32	metaperiodate as oxidant on silicagel and potassium permanganate as promotor	alkenes	acids	
26,33-36	cerium(IV) salts on silicagel	hydroquinones and catechols	quinones	
37,38	selenium dioxide on silicagel	allylic compounds with butylhydroperoxide in hexane or dichloromethane as solvent	allylic primary alcohols and α, β -unsaturated aldehydes	oxidation of allylic methyl group

Ref. No.	Catalyst	Reactants	Products	Remarks
39-42	cobalt oxide and complexes supported on silicagel	n-hexane	carbon dioxide and water	Total oxidation of n-hexane vapours in air to reduce air pollution, Temperature 553K
43,44	Iron complex immobilized on imidazole modified silicagel, Zn as reducing agent	alkanes and O_2 from methane monooxygenase enzyme, methylviologen as mediator and acetic acid as effector	ketones and aldehydes	
45,46	platinum on silicagel	n-hexane	ketones and acids	temperature 698-750K, pressure 3 atm and catalyst 4% Pt/SiO ₂
47,48	rhodium and rhodium-copper on silicagel	hexane and cyclohexane		
49	Vanadium supported on silicagel	isopropanol and n-hexane oxygen(1-) hole site		reaction is carried in UV
50	Iron-phthalocyanine encaged in zeolites	n-alkanes		
51-64	Titanium silicalite and vanadium silicate zeolites	n-hexane, cyclohexane and other n-alkanes with hydrogen peroxide	secondary and tertiary alcohols and ketones	
65,66	Titanium supported on modified mor-denite clay	saturated hydrocarbons, benzene and cyclohexane with hydrogen peroxide	alcohols and ketones	Solvents used were methanol and water. n-hexane in methanol gives higher conversion

Ref. No.	Catalyst	Reactants	Products	Remarks
67	Activated charcoal	n-hexane		Charcoal was chemically activated and treated at very high temperature with oxidizing agent. The reaction was carried out with and without UV
99	Transition metal complexes on polymer	olefins	epoxides	
103,104	Ziegler-Natta catalyst on polymer		polymer	Catalyst for polymerization
105	Immobilized polymer bound imidazole copper(II) catalyst	2,4-dimethyl phenol	polymer	oxidative coupling polymerization
106,107	Polymer bonded metalloporphyrins	alkanes with hydrogen peroxide	alcohols	Hydroxylation of saturated hydrocarbons
108	Manganese(II) tetraarylporphyrins	Alkanes and cycloalkanes oxidised by hydrogen peroxide		lypophylic carboxylic acid as promotor
109	Heteropoly salts with surface acid layers			acid-base and oxidation catalyst
110-113	Iron(III)porphyrin	Saturated hydrocarbons and alkanes oxidised with sodium hypochlorite	alcohols	Phase transfer catalysis

Chapter 2

Experimental

2.1 Preparation of Polymer Beads with Salicylaldehyde Schiff base

2.1.1 Preparation of Polymer Beads

Styrene-divinylbenzene co-polymer beads were prepared by the technique of suspension polymerization as described in reference[72]. Organic phase was prepared by mixing together toluene(50ml), styrene(70 g), divinylbenzene(20 g), and azobis-isobutyronitrile(1 g AIBN). This organic phase was suspended in an aqueous solution containing water(25 g), sodium sulphate(24 g), gelatin(0.007 g) and calcium carbonate(12 g). Suspension polymerization was carried out under controlled stirring at $60 \pm 2^\circ \text{C}$ for four hours. After this time, in order to make beads mechanically strong, the mass was heated to 90°C for one hour. these beads were then separated, washed with water and with acetone, and were dried in oven kept between $70 - 80^\circ \text{C}$. During experimentation, Gelatin content in aqueous phase was found to play an important role in controlling the bead size and the recipe given above gives beads of mesh size 10-20.

2.1.2 Chloromethylation of beads

Chloromethylation of beads was carried out using the technique described in reference [112]. A stock solution consisting of 90 g(3 mole equivalent) paraformaldehyde, methanol 250 g(3 mole equivalent) and HCl (35%, 225ml) was prepared. 10 g of beads were mixed with 150 ml of this solution and refluxed for 48 hours. The beads, after chloromethylation were found to become light yellow in colour. Chloromethylated beads are represented as P - CH₂Cl.

2.1.3 Reaction with diethanolamine

Thus prepared beads were reacted with diethanolamine (10 g of beads with 3 g of diethanolamine in solution with excess of chloroform) and refluxed for twenty four hours. These were refluxed further for three hours in presence of pyridine. This recipe is based on reference[68,77] and this leads to the formation of A as shown in the figure 2.1. The beads were found to turn cream in colour from light yellow.

2.1.4 Formation of Schiff base site

L - tyrosin (2 g) was dissolved in methanol by adding thionyl chloride (3-4 ml.) dropwise in ice cold condition. Beads (10 g) were added to this and the mixture was stirred in ice cold condition for 4 hours. It was further stored in cold water for about 24 hours and then washed with methanol. As a result of this, the beads underwent following modifications. The resultant beads were of light pink in colour and were mixed with N/10 NaOH and the mixture was refluxed for about 4 hours to remove HCl. The beads were then washed with water to give C below. Salicylaldehyde (2 ml) and these beads were then mixed in ethanol and kept in cold condition (0°C) for 8 hours. This gave rise to the formation of Schiff base functional group upon it by the following reaction.

2.1.5 Preparation of Cobaltous Palmitate

On mixing of palmitic acid (25 g, 0.1 mole) dissolved in 150mL ethanol (95%) and NaOH (4 g, 0.1 mole) in ethanol (75 mL), white precipitate of sodium palmitate was formed.

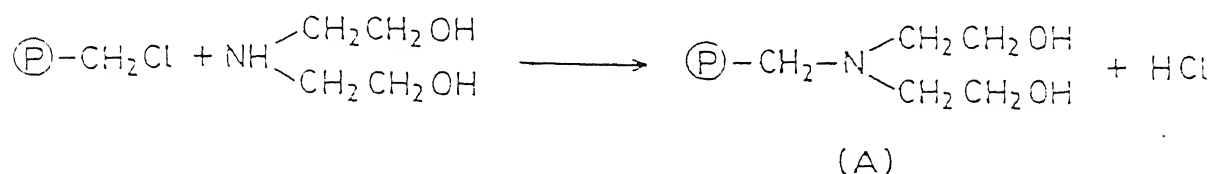


Figure 2.1: Amination reaction of Chloromethylated beads

Dried sodium palmitate (56 g, 0.2 mole) was dissolved in water at 60°C and to this was added the clear solution of cobaltous chloride (13 g, 0.1 mole) in water. The cobaltous palmitate appeared as purple precipitates. This was filtered, washed with methanol and air dried for 6 hours.

2.1.6 Loading of Cobaltous palmitate on Polymer Beads

Cobaltous palmitate (4 g) was dissolved in n-octanol (50 mL) by slowly heating at 60°C. 10 g beads were taken and mixed with this and refluxed for 20 hours. After this, the beads were separated and washed with 95% ethanol (100 mL) followed by acetone (100 mL). These were then dried in the oven for 4 hours. The beads became greenish in colour indicating the chelation of metal with the Schiff base site and were expected to have the formula shown in figure 2.5. To confirm that the chelation does not occur on phenyl residues, we similarly refluxed the macroporous beads without these active functional groups. We found no chelation of metal upon them.

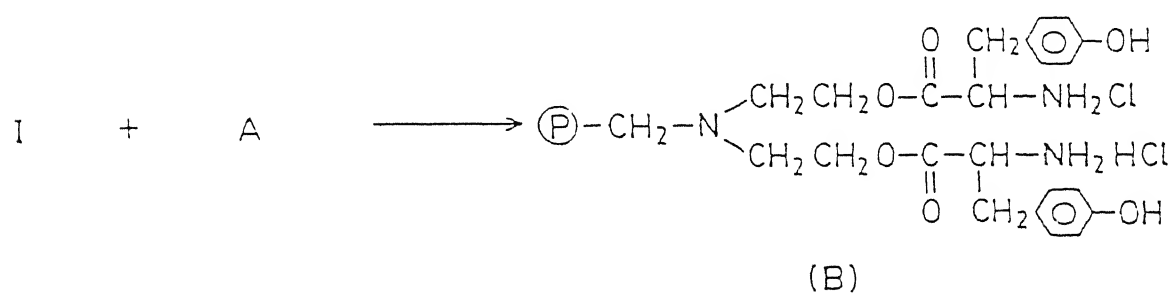
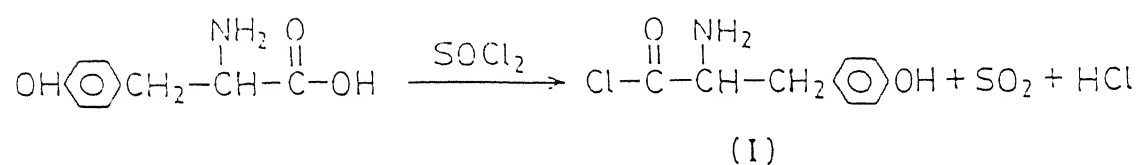


Figure 2.2: Reaction of polymer beads with L - Tyrosin

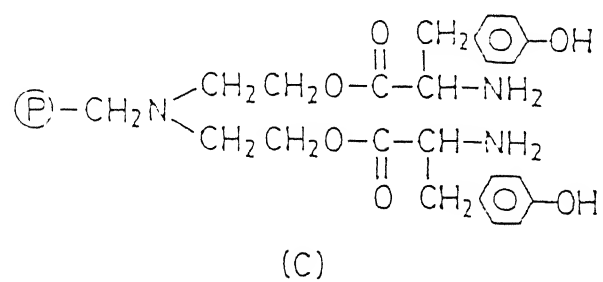


Figure 2.3: Polymer beads after washing with water

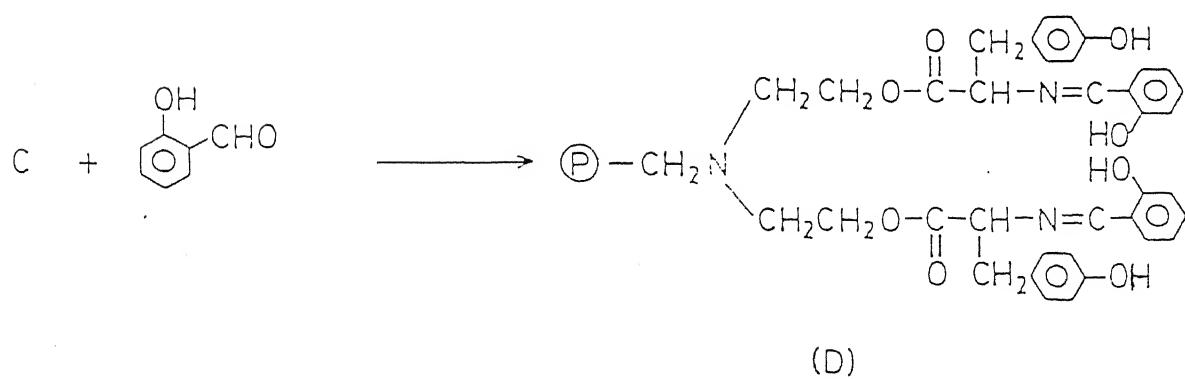


Figure 2.4: Schiff base formation on polymer beads with salicylaldehyde

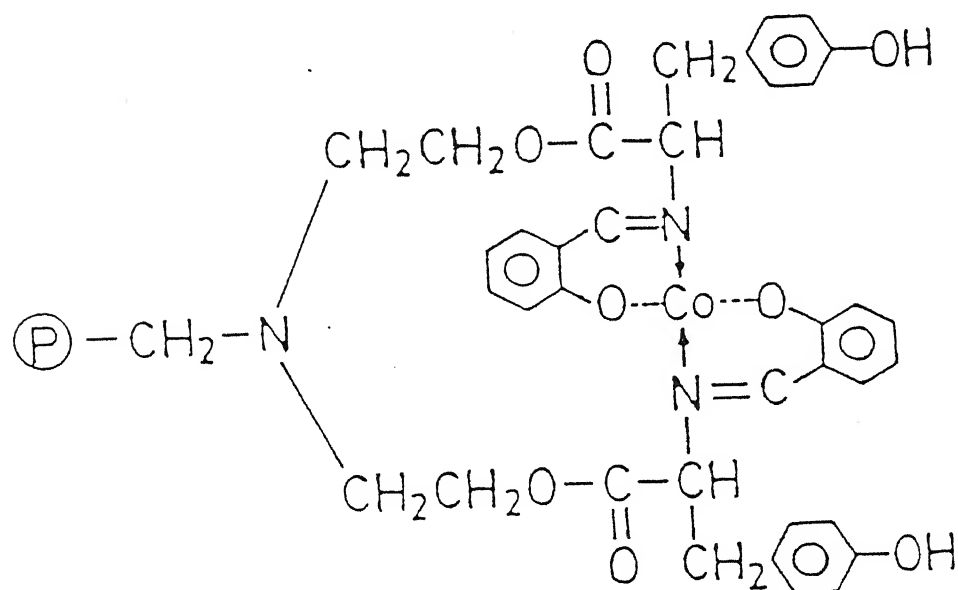


Figure 2.5: Structure of final metal complex supported catalyst

2.2 Measurement of Internal Surface Area

Measurement of internal surface area of polymer beads was made using standard BET isotherm apparatus (Micromeritics' Pulse Chemisorb 2700). This instrument works on a simple principle of BET adsorption isotherm.

2.2.1 Principle

One form of the well-known BET equation that describes the physical adsorption of a gas upon a solid surface is:

$$(P/P_{\infty})/V[1 - (P/P_{\infty})] = 1/(V_m C) + [(C - 1)/(V_m C)]P/P_{\infty} \quad (2.1)$$

where V is the volume (at standard temperature and pressure, STP) of gas adsorbed at pressure P , P_{∞} the saturation pressure which is the vapour pressure of liquified gas at the adsorbing temperature, V_m the volume of gas (STP) required to form an adsorbed monomolecular layer, and C a constant related to the energy of adsorption.

The surface area S of the sample giving the monolayer adsorbed gas volume V_m (STP) is then calculated from

$$S = V_m A N / M \quad (2.2)$$

where A is the Avogadro's number which expresses the number of gas molecules in a mole of gas at standard conditions, M the molar volume of the gas, and N the area of each adsorbed gas molecule.

The constant C of the equation 2.4 is typically a relatively large number, i.e., $C \gg 1$, from which equation 2.4 reduces very nearly to

$$(P/P_{\infty})/V[1 - (P/P_{\infty})] = (1/V_m)[(1/C) + (P/P_{\infty})] \quad (2.3)$$

Now if $P/P_{\infty} \ll 1/C$, equation 2.6 can be further represented by

$$(P/P_{\infty})/V[1 - (P/P_{\infty})] = (1/V_m)(P/P_{\infty}) \quad (2.4)$$

$$V_m = V[1 - (P/P_{\infty})] \quad (2.5)$$

Another way of arriving at the same result is by recognizing that the term $(1/V_m C)$ of equation 2.4 is generally small. Taking it as insignificant changes the slope, and hence the value of V_m and the sample surface area as calculated by equation 2.5, only a small amount. Equation 2.4 can be rearranged with the contribution of intercept term taken to be vanishingly small to give also

$$V_m = V[1 - (P/P_{\infty})] \quad (2.6)$$

Substituting equation 2.8 into equation 2.5 yields

$$S = V A N [1 - (P/P_{\infty})] / M \quad (2.7)$$

from which the sample surface area is readily determined once the volume of gas adsorbed (or desorbed, which must be identical) is measured and appropriate values for the other terms are incorporated.

For nitrogen gas adsorbed from a mixture of 30 mole % nitrogen and 70 mole % helium using a liquid nitrogen bath, the values are arrived at as follows:

- The volume V of the gas with which the Pulse Chemisorb 2700 is calibrated is injected at room temperature and the prevailing atmospheric pressure. This volume must thus be multiplied by the ratios $273.2/(\text{Rm. Temp. K})$ and $(\text{Atm. Press., mm Hg})/760$ to convert it to standard conditions (0°C and 760 mm Hg).
- Avogadro's number is 6.023×10^{23} molecules/g-mole.
- The presently accepted value for the area N of a solid surface occupied by an adsorbed nitrogen molecule is $16.2 \times 10^{-20} \text{ m}^2$ ($=16.2 \text{ Angstroms}^2$).
- The molar volume M of a gas at standard conditions is $22414 \text{ cm}^3/\text{g-mole}$.
- P is $0.3 \times$ the atmospheric pressure in millimeters of mercury since the gas mixture is 30% nitrogen and adsorption takes place at atmospheric pressure. P_∞ , the saturation pressure of liquid nitrogen is typically a small amount greater than atmospheric due to thermally induced circulation, dissolved oxygen, and other factors. With fresh, relatively pure liquid nitrogen, the saturation pressure is about 15mm Hg greater than atmospheric pressure. It can be 40 to 50 mm Hg greater if the liquid nitrogen is relatively impure. The saturation pressure should be determined by other means in the latter event.

The result for a 30% N_2 /70%He mixture adsorbed at liquid nitrogen temperature when the room temperature is 22°C and atmospheric pressure is 760mm Hg is the expression

$$S = V * Constant \quad (2.8)$$

where S is the surface area in square meters.

For calibration purposes, this means that a syringe injection of $V = 1.00 \text{ cm}^3$ of nitrogen at 22°C and 760mm Hg results in a constant having a value of 2.84. The value of S from equation 2.10 changes when ambient conditions differ significantly, the pressure changes being more effective i than temperature.

2.2.2 Procedure

To determine the internal surface area of the catalyst sample, using the above technique, following stepwise procedure should be adopted. *Calibration* : As discussed in the principle, for calibration purposes at the above specified conditions, the value of detector reading should be 2.84. To calibrate the instrument, first start the required carrier gas flow rate in the ratio 30% N_2 and 70% He. Then, switch on the instrument. Immediately, the detector reading will start fluctuating. Let this reading come to a steady value. Then inject 1.00 cm^3 of nitrogen gas in the circuit. This will start fluctuations in the detector reading and it will lead to a new steady value of the same after some time. This value, theoretically should be equal to 2.84. If this is not so, then adjust the same with the calibration knob at 2.84.

Sample preparation : The sample, the area of which is to be measured, should be free from moisture and other volatile impurities. The sample is filled in the dry sample holder, and the flow of carrier gas is passed through it. Heating of the sample is done above $100^\circ C$ with the help of heating mantle provided. Keep the sample for heating upto 30-45 min. to ensure complete removal of moisture and volatile impurities.

Measurement of surface area : Carrier gas in the above mentioned ratio of N_2 and He is passed through the sample. Here, the nitrogen is as an adsorbate gas and helium is as a carrier gas. Before starting the adsorption sequence, press the RESET button to make the detector reading zero. Then start the adsorption of nitrogen on the sample by immersing the sample holder in to liquid nitrogen bath kept at a very low temperature ($-197^\circ C$). After 5-7 min. of the immersion of the sample in liquid nitrogen, the detector reading starts fluctuating. This suggests the adsorption of nitrogen gas on to the surface of the sample. After about 30-45 min. the detector reading will reach a steady value. This steady state value is the surface area of the sample in square meter. As discussed in the principle, the area after the adsorption and desorption should be equal. This fact provides one an opportunity to check the obtained value of surface area by adsorption. Press the 'RESET' button and make the detector reading zero. Then remove the liquid nitrogen bath and allow the sample to come to the room temperature. this will tend to desorb the nitrogen that is adsorbed during adsorption. Again, the detector reading will start fluctuating and will lead to a steady state value. This value should be nearly equal to the value obtained by adsorption method. There may be a small difference in these two values due to the fact

that adsorption/desorption processes show hysteresis.

2.3 Preparation of Polymer Beads with Salen structure

2.3.1 Preparation of Polymer Beads

Styrene-divinylbenzene co-polymer beads were prepared by the technique of suspension polymerization as described above.

2.3.2 Chloromethylation of beads

Chloromethylation of beads was carried out using the technique described in reference [112] as above. Chloromethylated beads are represented as $P - CH_2Cl$.

2.3.3 Formation of Salen[N,N-ethylenebis (salicyldiminato) dianion] and Salphen(N,N-disalicylidene-o-phenylenediamine)

In this reaction, one mole equivalent of ethylenediamine(25 g) was reacted with two mole equivalent of salicylaldehyde(50 ml) by condensation reaction in 95% ethanol(100 ml) as solvent. The reaction mixture immediately gives Canary yellow precipitates of Salen on addition of reactants. reaction occurs as shown in figure 2.6.

One mole equivalent of o-phenylenediamine(25 g) was reacted with two mole equivalent of salicylaldehyde(50 ml) by condensation reaction in 95% ethanol(100 ml) to give Salphen. Reaction mixture was kept under controlled stirring for about one hour after which the yellowish orange precipitates of Salphen appears and reaction can be represented as shown in figure 2.7.

2.3. PREPARATION OF POLYMER BEADS WITH SALEN STRUCTURE 8

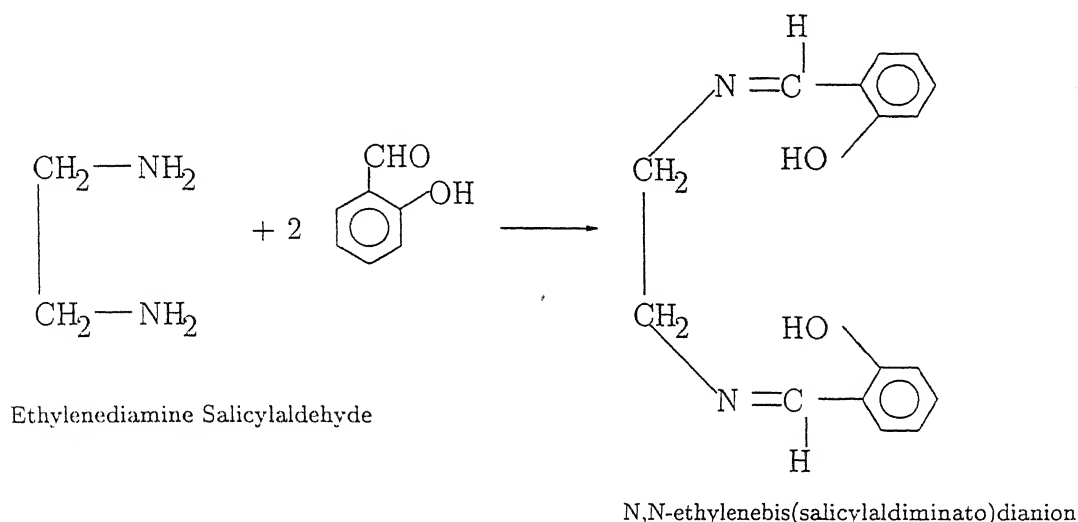


Figure 2.6: Formation of Salen

2.3.4 Introduction of Salen/Salphen to polymer beads

The above prepared Salen or Salphen is then introduced in the polymeric macroporous structure of co-polymer beads by introducing some modification in the technique described in reference [114]. Salen or Salphen (10 g) was dissolved in chloroform (50 ml), 10 g of chloromethylated beads and stannic chloride (2.5 g) were added to this solution and refluxed for 20 hours. After the reaction the beads were found to turn bright yellow in colour, confirming the introduction of Salen/Salphen in the pores of the beads.

2.3.5 Loading of Cobalt acetate in the Schiff base Salen/Salphen structure

Cobalt acetate (4 g) was dissolved in methanol (50 ml) at room temperature. 10 g of polymer beads with Salen/Salphen on it, were taken and added to this solution and refluxed for 20 hours. The beads were then separated and washed with 95% ethanol (100 ml) and subsequently with acetone (100 ml). These beads are, then dried in oven for 4 hours at around $60 - 70^\circ \text{C}$. The beads were found to become pinkish in colour, confirming the chelation of metal complex on the Schiff base site generated in Salen/Salphen and is expected to have structure as shown in figure 2.9.

2.3. PREPARATION OF POLYMER BEADS WITH SALEN STRUCTURE 9

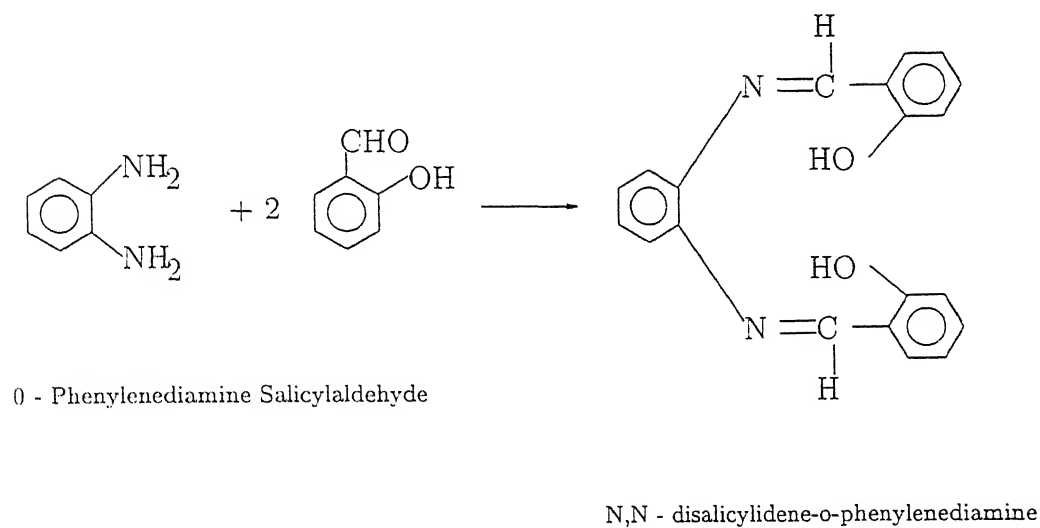


Figure 2.7: Formation of Salphen

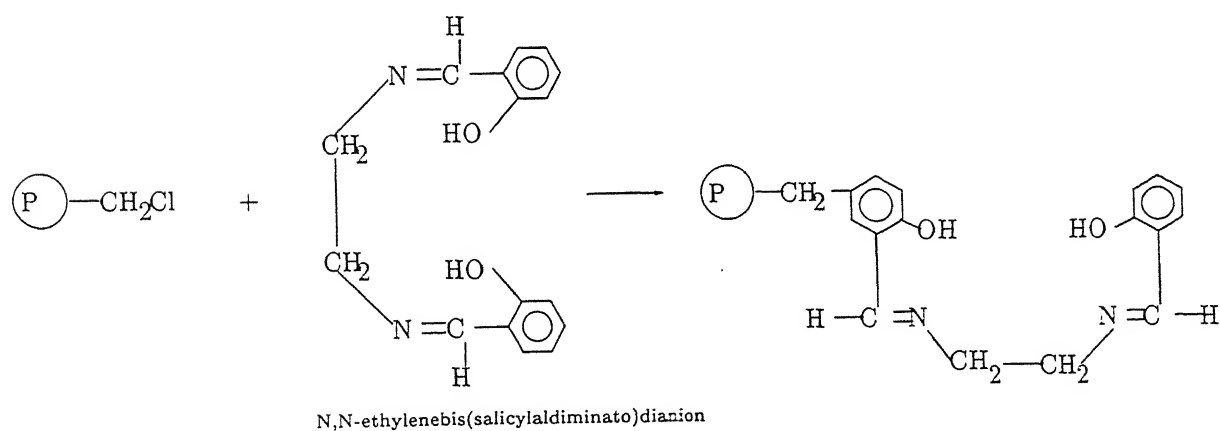


Figure 2.8: Introduction of Salen/Salphen to polymer beads

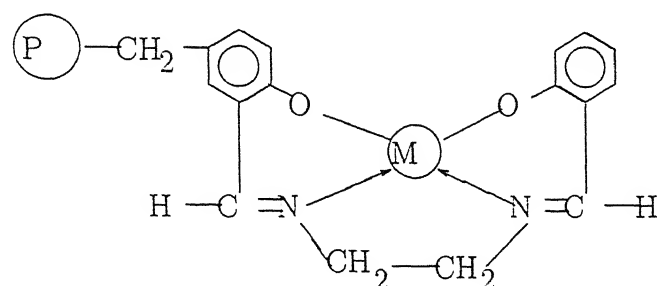


Figure 2.9: Structure of metal complex supported polymer catalyst

To confirm our claim that chelation does not occur on phenyl residues, we similarly refluxed these macroporous beads without introducing Salen/Salphen. We found no chelation of metal complex, thus confirming our claim.

As shown in figure 2.9, the metal complex is expected to have been bound by two ionic bonds with oxygen and two co-ordinate covalent bonds with nitrogen. This type of bonding firmly holds the metal complex on the site and rules out all chances of metal ion getting leached out during oxidation reaction, which is one of the most severe problem faced while carrying out reaction heterogeneously.

2.4 Preparation of Silica Gel supported Cobalt-acetate catalyst

Fresh silicagel was taken and was crushed manually and range of 10-20 mesh particle size silicagel was separated by sieves. It was then activated for 24 hours in an oven at around 80-90°C to remove moisture. A solution was prepared by dissolving Cobalt acetate(5 g) in methanol(100 ml) at room temperature. Activated silicagel(50 g) was added to this solution and was refluxed for 20 hours. At the end of this time, the silicagel was found to have undergone a colour change from blue to deep violate. This was separated and washed 3-4 times with methanol(50 ml)and dried in an oven for 10 hours at around 80-90°C.

2.5 Oxidation of n-Hexane

Experiments on the oxidation of n-hexane were carried out in a pressurised reactor which operated semibatchwise with oxygen available at constant pressure. The reaction apparatus consisted of 250 ml stainless steel(SS 304) autoclave equipped with a stirrer with having blades. The reactor has provisions for oxygen inlet, liquid sampling port and a pressure gauge with a range upto 300 psi.(20.4 kg/cm²) as shown in figure 2.10. Cooling coil is provided for controlling the reaction temperature for exothermic reactions. The speed of the stirrer is varied and the reactor can be heated externally by an electrical coil provided.

Experiments were conducted in a batchwise fashion, with respect to n-hexane, at constant pressure. Analysis of the products has been carried out using the gravimetric techniques described as follows [115,116].

2.6 Determination of hydroxyl groups

2.6.1 Discussion

Hydroxyl groups present in the sample can be readily acetylated by acetic (ethanoic) anhydride in ethyl acetate containing some perchloric acid. This reaction can be used as a basis for determining the number of hydroxyl groups in the sample by carrying out reaction with excess acetic anhydride followed by titration of the excess using sodium hydroxide in methyl cellosolve.

2.6.2 Solutions Required

Acetic anhydride. Prepare 250mL of a 2.0M solution in ethyl acetate containing 4.0g of 72% perchloric acid. The solution is made by adding 4.0g (2.35mL) of 72% perchloric acid to 150mL of ethyl acetate in a 250mL graduated flask. Pipette 8.0mL of acetic anhydride into the flask, allow to stand for half an hour. Cool the flask to 5°C, add 42mL of cold acetic anhydride. Keep the mixture at 5°C for 1 hour and then allow it to attain room

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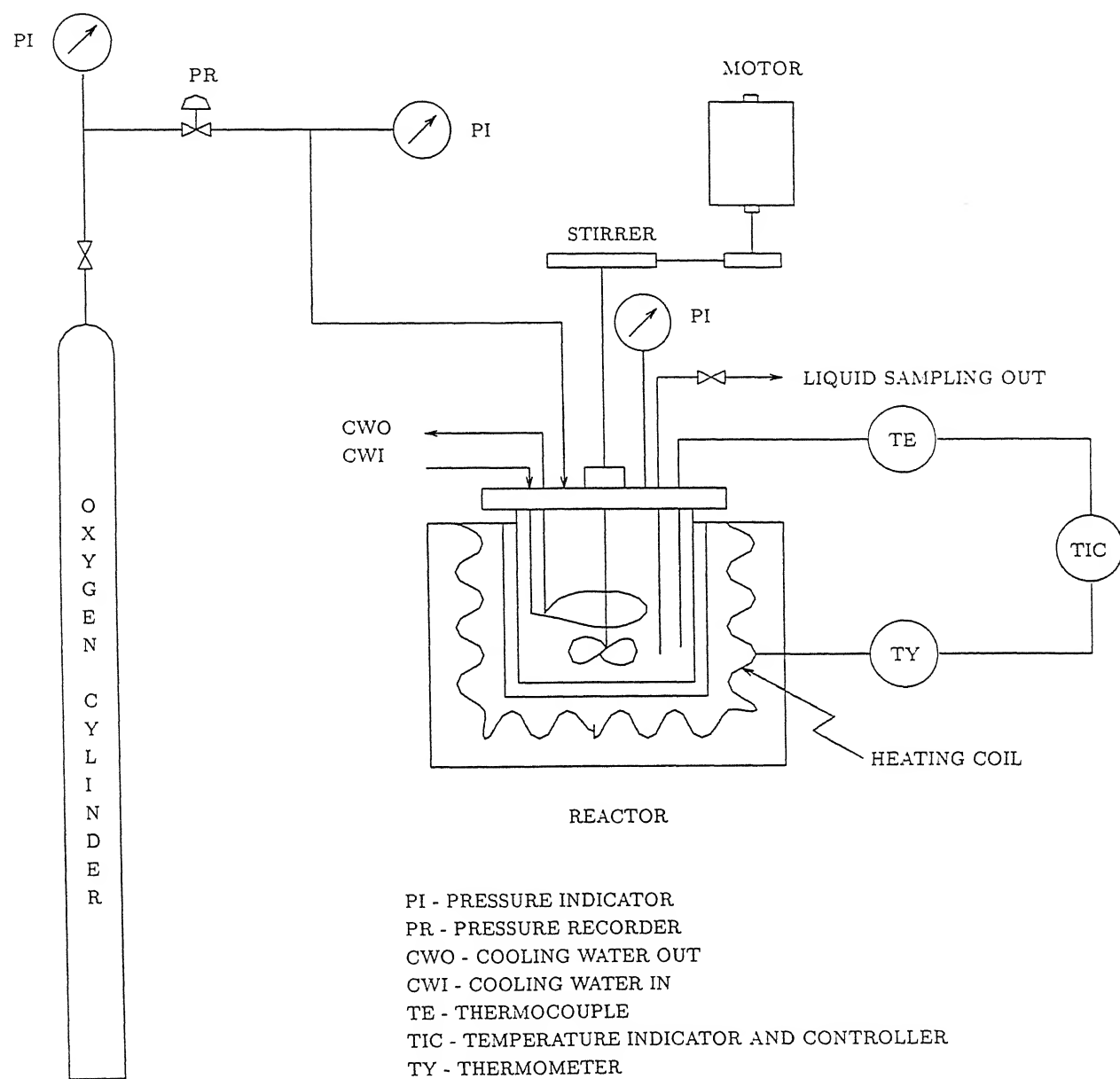


Figure 2.10: Schematic Diagram of Reaction Setup

temperature¹.

Sodium hydroxide. Prepare a solution of approximately 0.5M sodium hydroxide in methylcellosolve. This should be standardised by titration with potassiumhydrogenphthalate using mixed indicator given below.

Pyridine/water. Make up 100mL of a mixture formed from pyridine and water in a ratio of 3 parts to 1 part by volume.

Mixed indicator. This should be prepared from 1 part of 0.1% neutralised aqueous cresol red and 3 parts of 0.1% neutralised thymol blue.

2.6.3 Procedure

Weigh out accurately between 0.15g and 0.2g of the sample into a 100mL stoppered conical flask. Pipette into the flask exactly 5.0mL of the acetic anhydride/ethyl acetate solution. **Do not heat the solution.** Add 1.5mL of water and swirl to mix the contents, then add 10mL of pyridine/water solution, mix by swirling and allow the mixture to stand for 5 minutes. Titrate the excess acetic anhydride with the standardised 0.5M sodium hydroxide using the mixed indicator to give a colour change from yellow to violat at the end point.

Carry out a blank determination on the acetic anhydride/ethyl acetate solution following the above procedure without adding the sample. Use the difference between the blank, V_b , and the sample titration, V_s , to calculate the number of hydroxyl groups in the sample².

2.6.4 Calculation

The volume of 0.05M NaOH used is given by $(V_b - V_s)$, so the number of moles of acetic anhydride used in reaction with hydroxyl group is:

$$\frac{(V_b - V_s) * 0.5}{2 * 1000} \quad (2.9)$$

¹All solutions should be freshly prepared before use. Perchloric acid solutions must not be exposed to sunlight or elevated temperatures as they can be **EXPLOSIVE**.

²The solutions from the titrations should be disposed of promptly after the determination has been carried out.

But each acetic anhydride molecule reacts with two hydroxyl groups, so the number of moles of hydroxyl groups is:

$$N = \frac{2(V_b - V_s) * 0.5}{2 * 1000} = \frac{(V_b - V_s)}{2000} \quad (2.10)$$

If the relative molecular mass(R.M.M.) of the sample is known, then the number of hydroxyl groups per molecule is given by:

$$\frac{N * R.M.M.}{G} \quad (2.11)$$

where G is the mass of sample taken.

2.7 Determination of ketone group by Hydrazone formation

Hydrazine react quantitatively with carbonyl compounds to form corresponding hydrazines. This procedure employs standard identification reaction of dinitrophenylhydrazine for carbonyl compounds. This reaction is essentially quantitative for many aldehydes and ketones, making the procedure quite generally applicable. This procedure is designed for water soluble samples only.

Reagents: The reagent used is a saturated solution at 0°C of 2,4 - dinitrophenylhydrazine in 2N aqueous hydrochloric acid solution. This solution contains about 4 mg. hydrazine per mL. The other reagent used is 2N hydrochloric acid solution.

Procedure: In a glass-stoppered flask, place 50mL. of reagent. To this add the sample, which should contain approximately 40×10^{-5} mole of ketone. Allow the mixture to stand in an ice bath for 1 hour. In the case of the volatile carbonyl compounds such as acetaldehyde or acetone, it is advisable to shake the flask vigorously from time to time to ensure the reaction of any carbonyl compound which may be in the atmosphere above the reagent. After the period of standing, filter the precipitate off into a sintered glass funnel. Wash the precipitates with 2N hydrochloric acid, then dry it in the oven at 100°C.

Calculations: The calculation of % of carbonyl compound is given as

$$\%carbonylcompound = \frac{weighthydrazone}{weightsample} * 100 \quad (2.12)$$

2.8 Oxidation of Paraffin Wax

The above prepared silicagel supported cobalt acetate was also used for the oxidation of paraffin wax (saturated straight chain hydrocarbon) using the molecular oxygen. Reaction was carried out in liquid phase at 150°C (melting point of paraffin wax is 61°C) and 100 psig. pressure, with 5 g catalyst and 0.5 g AIBN as promotor. The reaction was run for 7 hours. The products were analysed by the procedure later in this chapter.

During the analysis of the products, we found following difficulties.

- The paraffin wax, at room temperature, is solid (melting point = 61°C) so to carry out the analysis in the liquid phase we had to dissolve the sample in suitable solvent.
- Parrafin wax is sparingly soluble in most of the solvents.

After carrying out a some experiments on the solubility of wax in different solvents like chloroform, carbon tetrachloride, benzene, n-hexane etc., we have chosen n-hexane (AR Grade) as solvent in our case. We also have modified the analysis procedure for determination of hydroxyl group as follows.

The wax sample (5 g) is added in 100mL of n-hexane and kept for 24 hours to ensure the complete dissolution. This sample is then analysed for the hydroxyl group concentration using the procedure described earlier in section 2.5. The calculation of moles of hydroxyl group present in this (wax, dissolved in n-hexane) sample is carried out as described in the procedure. Now, we know the weight fraction of wax sample added in this solution. Since then-hexane we have used is AR grade, it is free from impurities. Then the moles of hydroxyl group determined by the above procedure is same as moles of that in wax sample. So dividing the obtained value by the weight fraction will give the moles of hydroxyl groups in wax per mole of sample.

Chapter 3

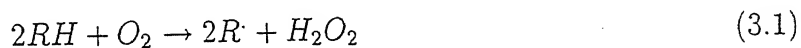
Mechanism of Alkane Oxidation

3.1 Autoxidation

Liquid phase oxidation of saturated hydrocarbons is a highly complex reaction, the mechanism of which is not fully known and understood. It is generally accepted that the oxidation of n-alkanes proceeds through homolytic pathways that involve formation of free radical intermediates[14,41]. The basic steps in the classic free radical chain mechanism for autoxidation of alkanes can be represented as follows.

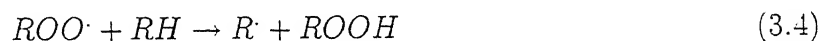
3.1.1 INITIATION

Initiation occurs by abstraction of hydrogen atom from the hydrocarbon molecule.



3.1.2 PROPAGATION

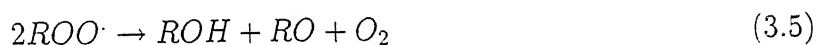
This step involves the rapid reactions of the different radicals with molecular oxygen followed by hydrogen abstraction from hydrocarbon to form an alkyl hydroperoxide and an alkyl radical to propagate the chain.



These reactions maintain the concentrations of free radicals and transfer the hydrocarbons to hydroperoxides.

3.1.3 TERMINATION

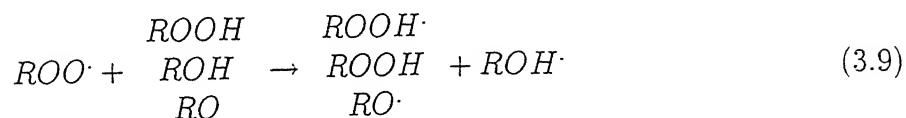
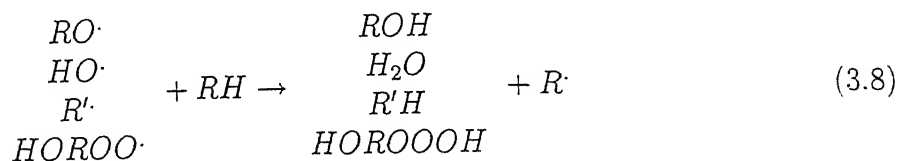
Termination of radical chains by the coupling of free radicals takes place as



Numerous other reactions can also occur. Hydroperoxides can decompose giving free radicals.



Various reactions, involving this, can take place in the propagation step are



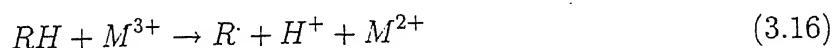


Reactions (3.5), (3.8) and (3.9) explain formation of alcohols, similarly reactions (3.5), (3.11), (3.13) and (3.14) explain ketone formation. Reaction (3.15) explains acid formation.

At elevated temperatures due to thermal decomposition alkyl hydroperoxides are easily oxidized to stable products such as alcohols, ketones and acids. Therefore it is preferred to carry out selective autoxidation of alkanes at low conversions under mild conditions with recycle.

3.2 Catalytic Oxidation

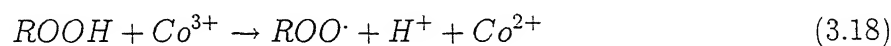
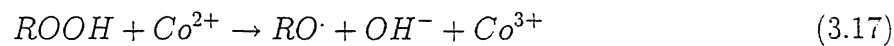
It is expected that the above mechanism is valid even in the presence of a metal catalyst. The catalyst provides alternate routes for the formation of different products. Thus numerous other reactions can also take place. An alternative initiation reaction can be



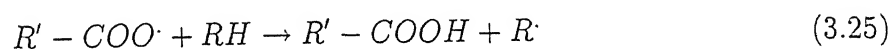
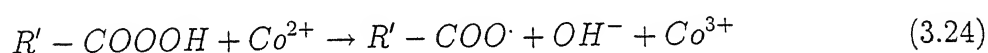
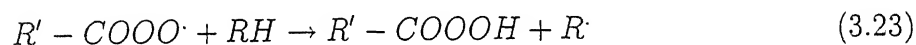
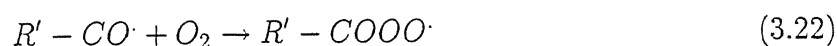
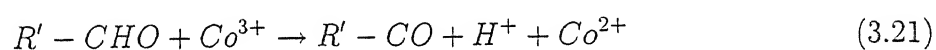
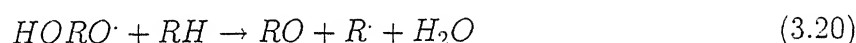
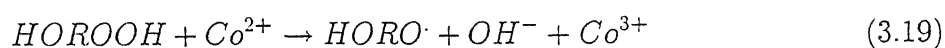
where $M^{3+} = Co^{3+}, Mn^{3+}$ etc. The primary effect of metal salts or metal complexes on liquid phase oxidation of alkanes is to increase the rate of reaction by catalysing the homolytic decomposition of hydroperoxides to give both, alkoxy radicals and alkyl peroxy radicals.

The cobalt catalyst can increase hydroperoxide decomposition according to following elementary steps.

3.2.1 INITIATION



3.2.2 PROPAGATION



Reactions (3.19) and (3.20) explain the formation of ketones previously described by eqn. (3.13). Equations (3.21)-(3.25) show the formation of acid. The chain degeneration of hydrocarbons ièautocatalytic nature is explained by eqn. (3.7) and (3.17).

Chapter 4

Results and Discussion

4.1 Characterisation of Polymer beads

Polymeric beads that we have formed are macroporous in nature because the medium of toluene is a good solvent for linear polystyrene chains. These beads have been characterised for their particle size distribution and internal surface area by varying the amount of different ingredients of the recipe given earlier. Among these ingredients, our experimental work revealed that nature of solvating medium (e.g. toluene in the recipe) and the amount of gelatin were the two most important components. In this work we carried out polymerization using n- heptane (non solvent to linear polystyrene) mixed with toluene as the solvating medium in varying ratios to determine its effect on internal surface area and particle size distribution of the beads formed. We have summarised our results on the former in table 4.1.

The internal surface area measurements were made using the procedure given in the experimental section. We observe that the emulsion polymerization technique of forming polymer beads does not work beyond 40% heptane and as the % heptane is increased, the internal pores are reduced.

In the presence of a solvating diluent, the formed beads are in a swollen state and its degree reduces by presence of a non solvent. In the case of a non solvating diluent, the polymer chains get more entangled and thus form a compact structure with lower internal

Percentage Heptane	Internal Surface Area (m^2/g)
0	9.331
10	6.328
20	5.027
30	3.862
40	Polymerization not possible

Table 4.1: Effect of nature of diluent on the Internal Surface Area

surface area. The particle size distribution were measured by sieving and results have been plotted in figure 4.1. The particle size distribution is extremely sharp and is found not to be affected by amount of non solvent (% heptane).

Next, we examined the effect of gelatin, used in the aqueous phase. Gelatin has been found to have great influence on the particle size as well as the internal sruface area of the beads formed. The experiments were conducted using different gelatin contents in each run. The experimental results are shown in figure 4.2 to 4.11. The particle size distribution obtained for each run was (figure 2.2 to 2.9) found to be extermely sharp. It was (figure 2.10) observed that increasing gelatin content reduces the average size of the beads. Our experimental results also show that there is a critical gelatin concentration, C_{crit} , below which beads are unstable and agglomerate to give a large polymer mass. In our case 0.017 g/120mL of water was this critical value.

Internal surface area of the beads formed is another property which is found to be greatly influenced by the amount of gelatin content in water of the recipe. We have shown the results in figure 4.11 and we find that the internal surface area increase with the increase in gelatin content. It must be observed that if this is used as catalyst in a tubular reactor or in a fixed bed reactor, reducing particle size would give higher pressure drop. From the two results of figure 4.10 and 4.11 we believe that there is an optimal value of gelatin content for which the average size of the particle and internal surface area, both give optimal performance. In our case for further development of catalyst we have chosen

Modified beads after...	Internal surface area
Chloromethylation	9.087
Amination	8.903
Reaction with L-tyrosin	9.113
Schiff base formation with salicylaldehyde	9.152
Metal complex loading	8.997

Table 4.2: Effect of modification on the Internal Surface Area of Polymer beads

value of gelatin content as 0.0275 g/120mL of water which gives average particle size of 1.163mm.

In the next stage of our work, we have subjected the beads to chloromethylation, amination, reaction with the aminoacids, Schiff base formation with salicylaldehyde and the metal complex loading. After each of these stages, we have characterised the beads for internal surface area. These modification reactions are a part of the procedure for catalyst preparation. The results are given in table 4.2. We find that the modification reactions on the polymer beads does tend to make any significant change in the surface area of the particles.

4.2 Preparation of Catalyst

Using those experimental data, the polymer beads of chosen size was prepared for the catalyst preparation. Beads of uniform size were separated by sieving and were subjected to chloromethylation as described in reference [70]. The bond formation of chlorine was confirmed by analysing the chloromrthylated beads using IR spectroscopy. The IR spectra of the same gave the peak corresponding to the bond formation of chlorine with carbon. The beads thus formed were found to have undergone a colour change from white to light

ytellow. These were then subjected to amination reaction, reaction with L - tyrosin and the Schiff base formation with salicylaldehyde in this order as described earlier. These were analysed for the success of the reaction after each of these above steps by IR spectroscopy. Thus prepared beads were also subjected to elemental analysis by Electron Probe Micro Analyser (EPMA, JXA-8600MX, Jeol) to give the different elements present on it. The results are attached in the appendix I and they are found to show the presence of carbon, nitrogen and oxygen in the sample confirming our claim.

The characterised beads were then loaded with Vanadium metal complex on it. The bright yellow beads were found to turn dark green after loading of the metal which is characteristic colour of vanadium metal (V^{4+}). This was analysed once again using Electron Probe Micro Analyser.

4.3 Oxidation Reactions

Experiments were conducted on the epoxidation of allyl chloride using the polymer supported Vanadyl catalyst. Reaction was carried out at 100°C and 85 psig pressure for 6 hours. The extent of reaction was found to be negligibly small as confirmed by gas chromatographic technique using column OV-I. Vanadium complex supported on polymer remained inactive in the presence of oxygen. We decided to use AIBN promotor in the next run. This time, instead of giving any oxidation product, the allyl chloride was found to undergo polymerization reaction giving a highly viscous reaction mass. We subsequently loaded cobalt palmitate on the polymeric beads. Experiments on the oxidation of n-butanol was carried out using these at 100°C and 85 psig pressure with and without promotor. The extent of reaction was found negligibly small as determined by gas chromatography. We also tried to carry out reaction at different temperatures and pressures with no effect. Next we tried oxidation of p-xylene and n-hexane which has been reported [115] to be catalysed by cobalt metal ion complexes but our catalyst did not give this reaction.

After this we decided to load the cobalt acetate on the beads but in the oxidation of n-hexane, it was getting leached even though high conversion was obtained. The leaching of the metal complex forced us to find a stronger chelating ligand for holding the metal complex on the bead. In this work we have selected Salen Schiff base as the complexing group on the polymer structure. Salen Schiff base was introduced on the polymer structure

Catalyst	% conversion
Cobalt acetate supported on polymer with Salen functional group	17.81
Blank cobalt acetate	29.73

Table 4.3: Comparison of conversions obtained from polymer supported and blank cobalt acetate

as described earlier.

4.4 Oxidation of n-Hexane

Experiments were conducted on the oxidation of n-hexane using the above prepared polymer beads having Salen group supporting cobalt acetate. The reaction was carried out at 100°C and 85 psig pressure with AIBN as promotor. The analysis of the product showed very high conversion of n-hexane as reported in table 4.3. The reaction products were alcohols along with a negligibly small amount of ketones suggesting a selectivity of almost 100%. We also carried out the oxidation of n-hexane using blank cobalt acetate (in powdery state, without any support), maintaining the same reaction conditions. To our surprise, it was determined that the use of blank cobalt acetate was giving much higher conversion of n-hexane as compared to the polymer supported cobalt acetate. These experiments suggest that the oxidation of n-hexane is influenced by either the nature of support or the metal complex. The reason for this lower conversion can be attributed to the diffusional resistance offered inside the pores of the polymeric structure. In view of this we examined other supports on the surface of which the cobalt acetate can be chemisorbed. After extensive search we finally decided to examine silicagel for support. Cobalt acetate was supported on silicagel as described earlier in chapter 2. Oxidation reactions on n-hexane were carried out at the same reaction conditions using molecular oxygen. After the analysis, we found that the conversion of n-hexane was higher compared to the previous two cases. This catalyst

was similarly specific and selective towards the formation of alcohols. The product mixture was also analysed by IR spectroscopy along with the reactant (n-hexane) for comparison. The results are as shown in appendix I. These two spectra, on comparison, suggest that the product mixture contains mostly alcohol and ketone in lesser amount.

4.4.1 Effect of Temperature

In order to study the effect of temperature on the oxidation of n-hexane, experiments were carried out at various temperatures in a batchwise fashion with respect to n-hexane and keeping other parameters constant (*viz.* oxygen pressure, catalyst and promotor concentrations and reaction time) in the presence of silicagel supported cobalt acetate. The results are reported in figure 4.12 where % hydroxyl functional group has been plotted as a function of temperature. It may be seen from the figure that the % conversion of n-hexane passes through a maxima at 80°C. Beyond this value of temperature the conversion is found to decrease which is a result indicating either a parallel reactions or the deactivation of catalyst. Since there was no other product formed, this maxima suggests later. At low temperature, the process of conversion of Co(II) to Co(III) and back to Co(II) is very slow. Low temperature is also not sufficient to bring about thermal oxidation of n-hexane.

4.4.2 Effect of Pressure

The reaction system is having three phases; gas, liquid and solid, with the product forming in the liquid phase only. The dissolved oxygen in the reaction medium is expected to play an important role in the oxidation reaction and with the increase in the oxygen pressure the solubility of the same is expected to increase. As a result the experiments were conducted at different pressures in the presence of the silicagel supported catalyst. The temperature of the reaction was fixed in these studies at the optimal value of 85°C obtained from the data presented in figure 4.13. The results are plotted in figure 4.5 and oxygen pressure is shown to be an important parameter in the oxidation process. From the figure it is seen that the curve again passes through a maxima, at around 85 psig. oxygen pressure. The initial increase in the conversion is justified as the solubility of oxygen increases with pressure. The decrease in the conversion at high pressure might be due to possible blocking of internal

pores of the catalyst and thus increased diffusional resistance offered to n-hexane.

4.4.3 Effect of catalyst loading

To determine the effect of catalyst loading on the conversion of n-hexane, the catalyst concentration in the reaction mass was varied. The temperature and pressure were chosen from the data obtained from previous two cases as 80°C and 85 psig. pressure. The results have been plotted in figure 4.14 as % conversion versus the amount of catalyst. This figure shows that with increase in the catalyst amount the conversion increases initially, but in the later stage it reaches an asymptotic value. When we used large amount of catalyst we faced following operational problem. With high catalyst/reactant ratio, the stirring was found to stop between the reaction.

4.4.4 Effect of Reaction Time

To determine the effect of reaction time on n-hexane, the oxidation reaction was carried out at chosen optimum reaction conditions (80°C, 85 psig. and 5.0 g catalyst). Samples were taken out at every two hours and analysed. The n-hexane conversion, as expected, increases with time and after 8 to 9 hours, it reaches a steady state value. This is shown in figure 4.15 as plot of % conversion as function of time suggesting that the oxidation is an equilibrium reaction.

4.4.5 Effect of recycling of the catalyst

To determine the recyclability of the catalyst and its effect on the conversion of n-hexane, the reactions were carried out at the optimum conditions, with reaction time of 7 hours. The same catalyst was used for 10 runs (total time of 70 hours) and the conversion of n-hexane was found to decrease steadily giving half the conversion after 10th run as shown in figure 4.16.

4.4.6 Effect of Promotor

To see the effect of promotor we carried out reaction at the chosen optimum conditions, but without adding the promotor (AIBN in our case). It was observed that the conversion of n-hexane was negligible without the use of promotor. This was due to the fact that Aibn at temperatures higher than the room temperature, gets decomposed and forms the free radicals. These free radicals are found to influence the initiation and propagation chain reactions as described in the reaction mechanism. Further, to detect the effect of concentration of promotor in reaction medium on the % conversion, we carried out reactions with varying amount of AIBN. It was observed that the amount of promotor in the reaction medium was not influencing the % conversion of n-hexane and has negligible effect on the kinetics of the reaction.

4.5 Oxidation of Paraffin Wax

The silicagel supported cobalt acetate was also used as catalyst for the oxidation of paraffin wax. We have examined the effect of temperature and time as variables affecting the kinetics of the reaction. It was observed from the analysis that the oxidation of paraffin wax produces hydroxyl groups only on it with no other functional group. The colourless molten paraffin wax was found to undergo a colour change to yellowish liquid after the reaction. It was also observed that in case of higher reaction time (10 - 11 hrs.) the liquid after the reaction becomes orange in colour and on solidification at room temperature gives a light brown pasty, grease like mass. The viscosity of the product mass was also observed to decrease at higher temperature and longer reaction times. This result can be attributed to the fact that at higher temperatures and longer reaction times the long hydrocarbons chains (C_{10} to C_{40}) present in paraffin must be undergoing breakage or rearrangement and forming lower order compounds with one or more hydroxyl groups attached to it. These runs have been carried out at different temperatures and the results are reported in table 4.4. This shows the moles of hydroxyl group in wax per mole of sample.

Temperature	Moles of Hydroxyl Group
100	0.112
120	0.0217
140	0.107

Table 4.4: Effect of Temperature on the Oxidation of Paraffin Wax

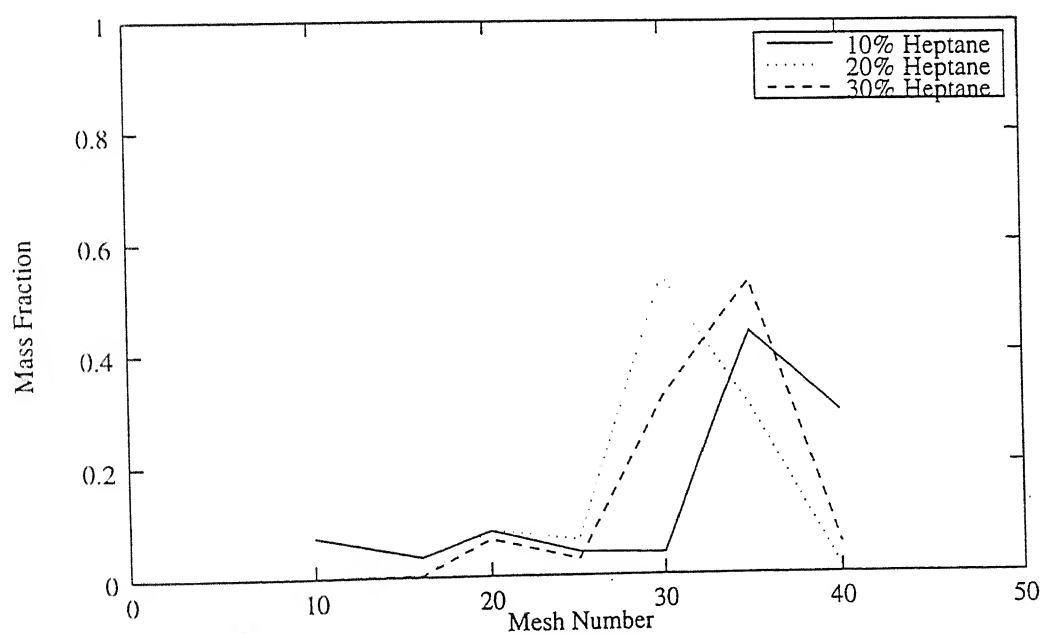


Figure 4.1: Effect of Nature of Diluent on particle size distribution of Polymer Beads

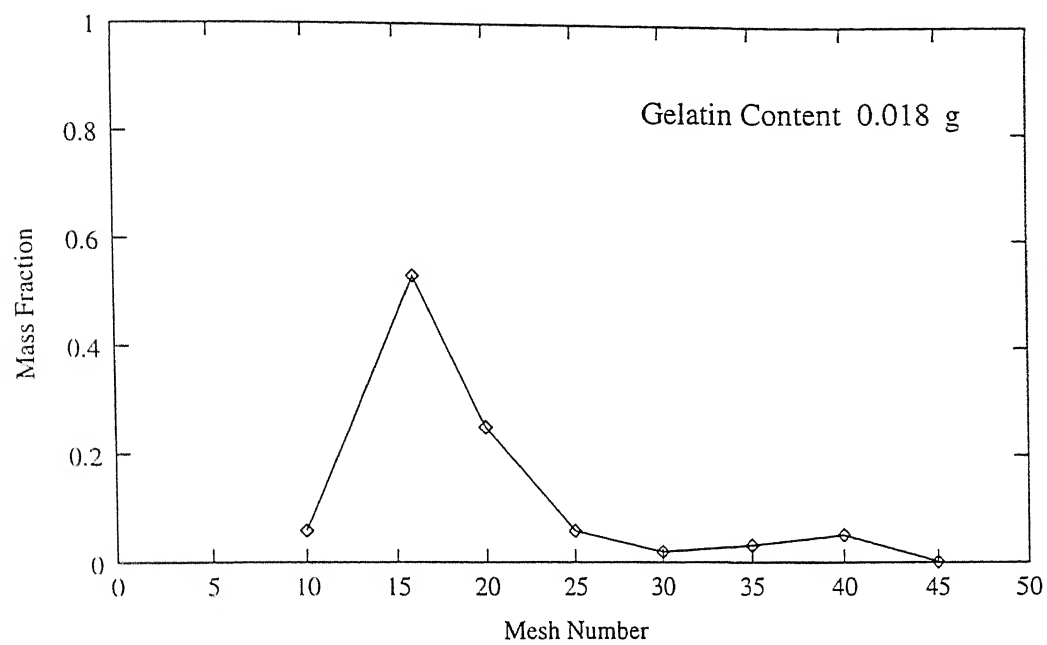


Figure 4.2: Particle size distribution : Gelatin content 0.018 g

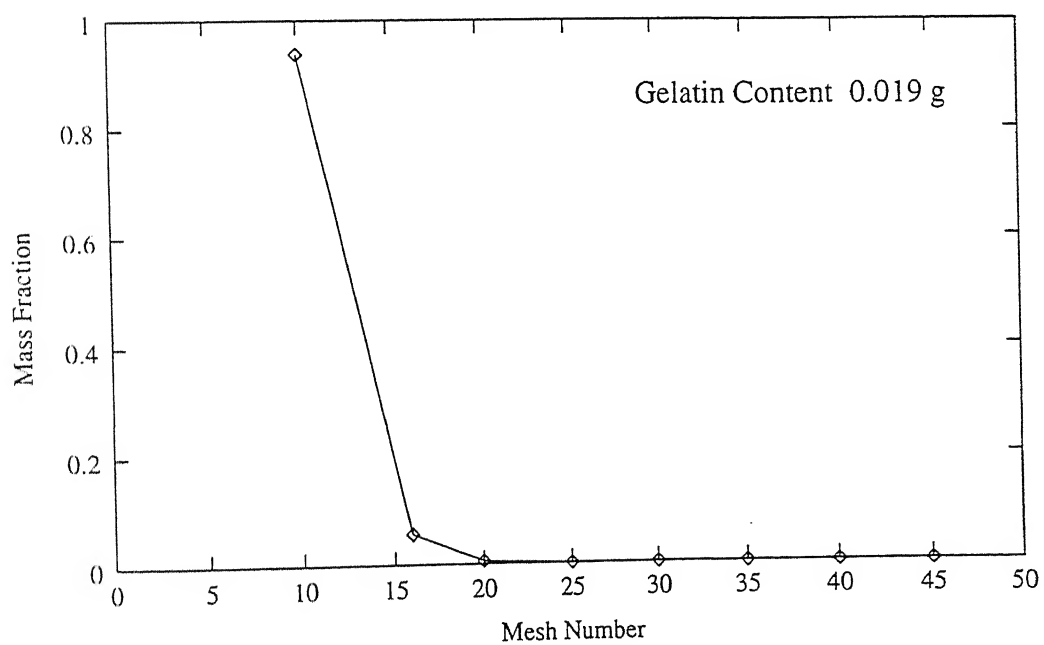


Figure 4.3: Particle size distribution : Gelatin content 0.019 g

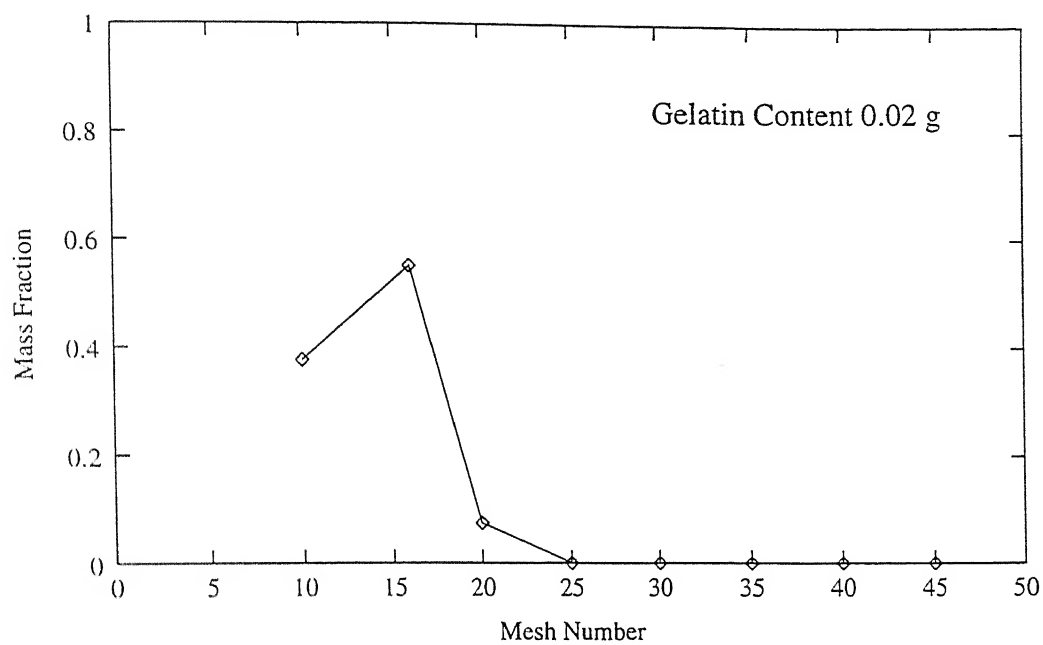


Figure 4.4: Particle size distribution : Gelatin content 0.020 g

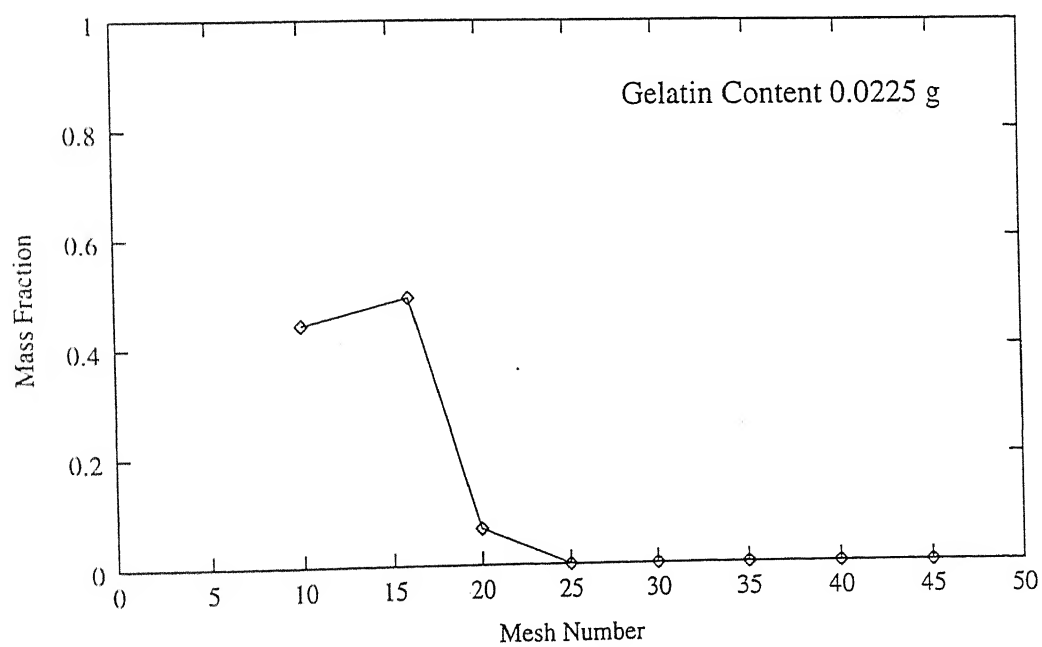


Figure 4.5: Particle size distribution : Gelatin content 0.0225 g

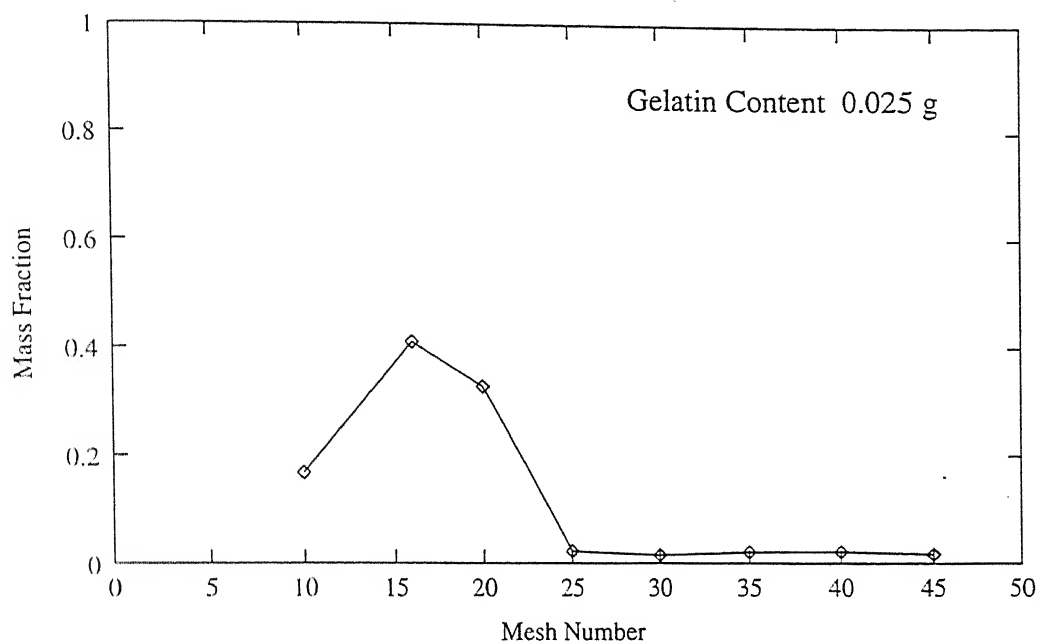


Figure 4.6: Particle size distribution : Gelatin content 0.025 g

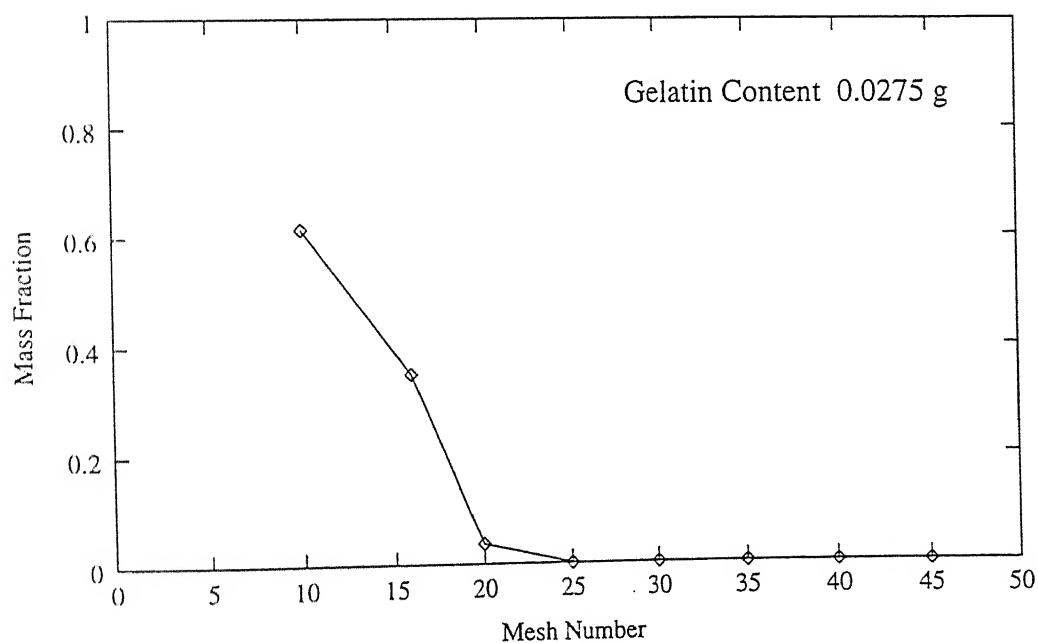


Figure 4.7: Particle size distribution : Gelatin content 0.0275 g

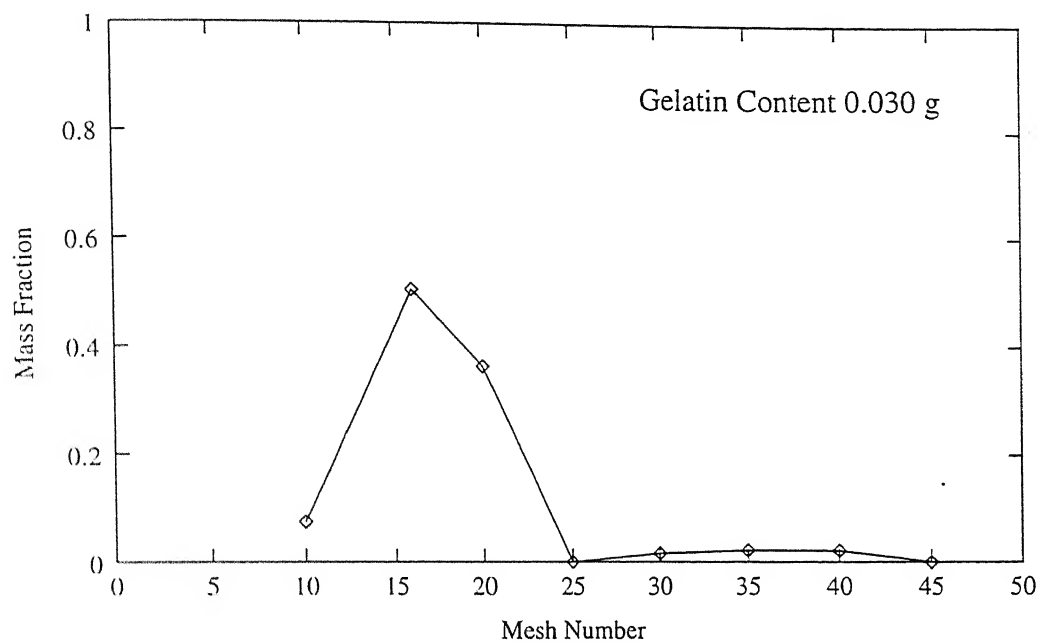


Figure 4.8: Particle size distribution : Gelatin content 0.030 g

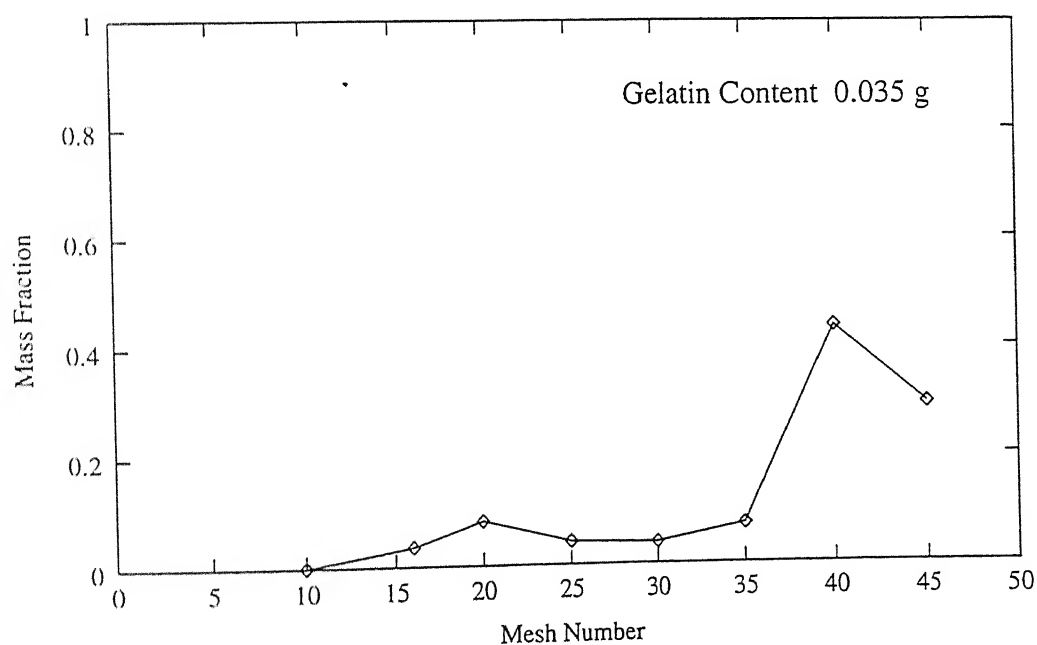


Figure 4.9: Particle size distribution : Gelatin content 0.035 g

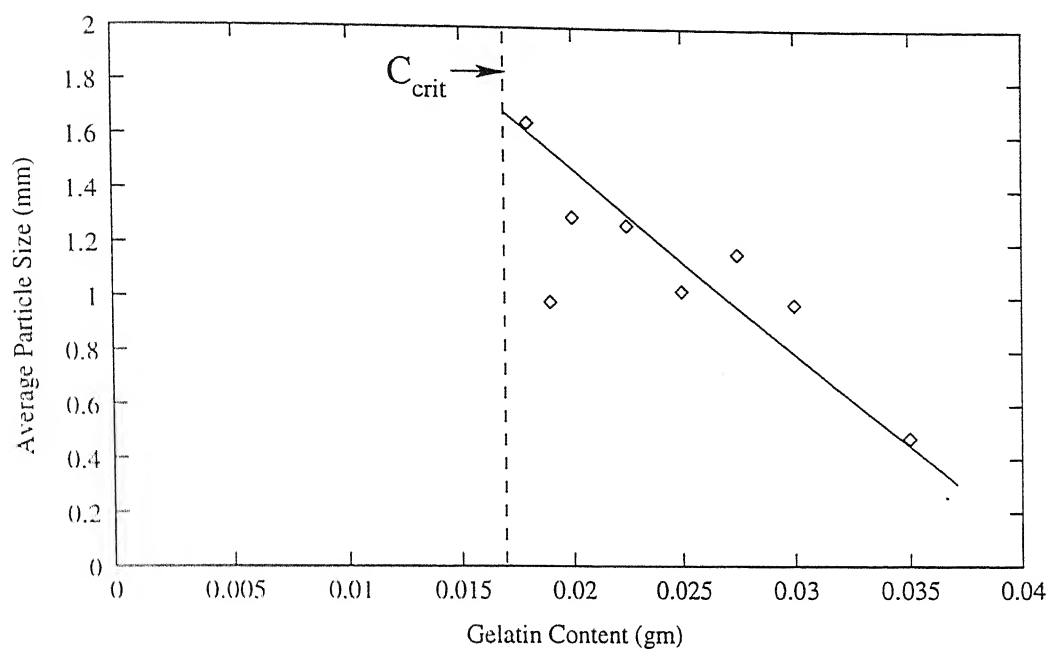


Figure 4.10: Effect of Gelatin content on Average Particle Size of Ploymer Beads

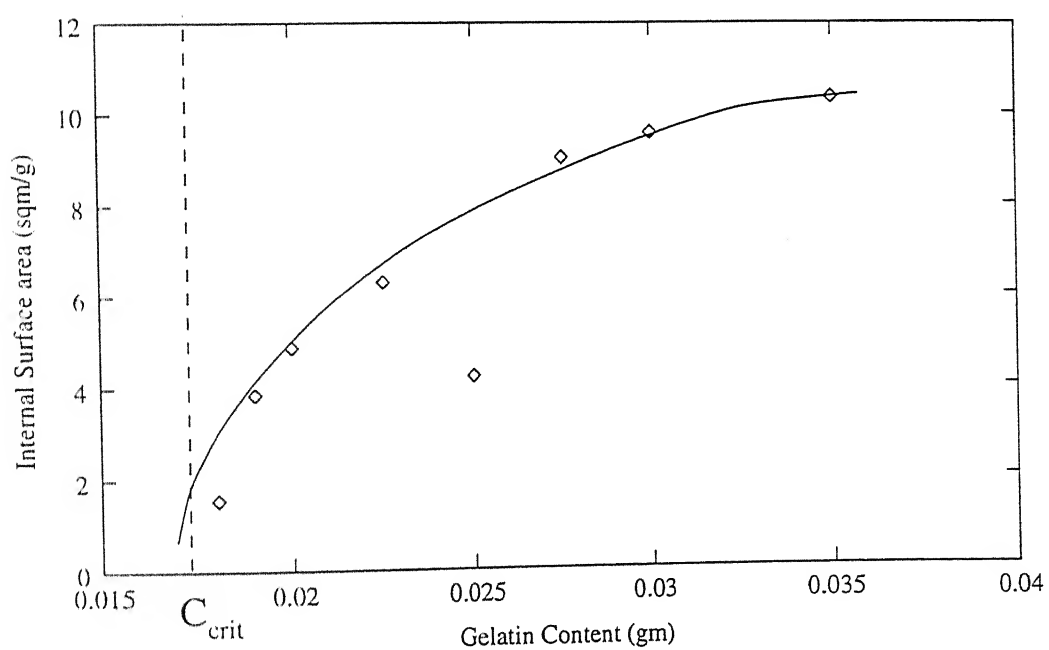


Figure 4.11: Effect of Gelatin Content on Internal Surface Area of Polymer Beads

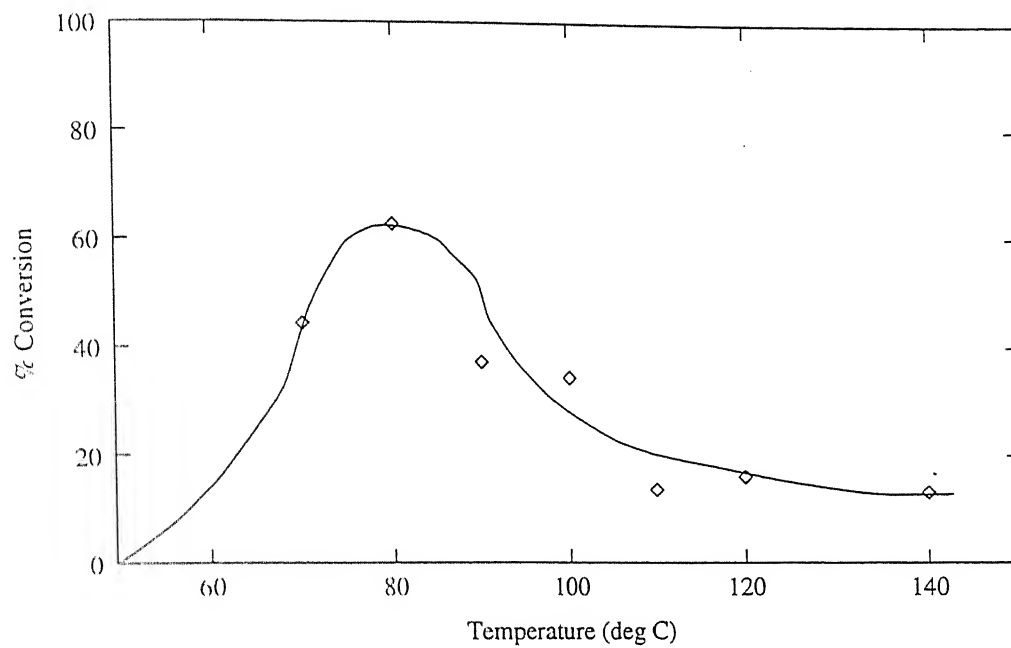


Figure 4.12: Effect of Temperature on % Conversion of n-hexane

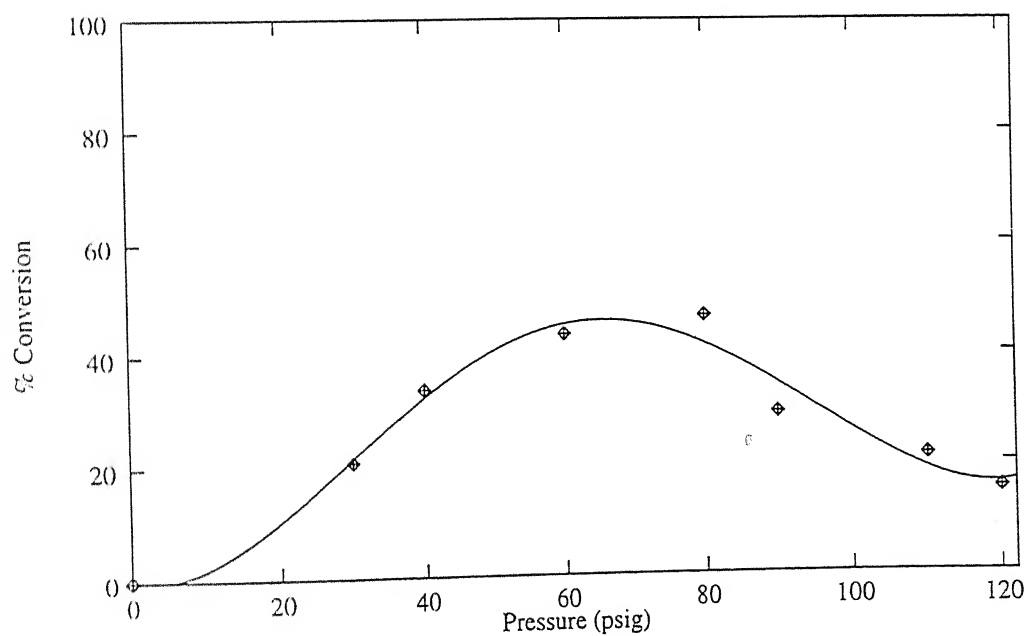


Figure 4.13: Effect of pressure on % Conversion of n-hexane

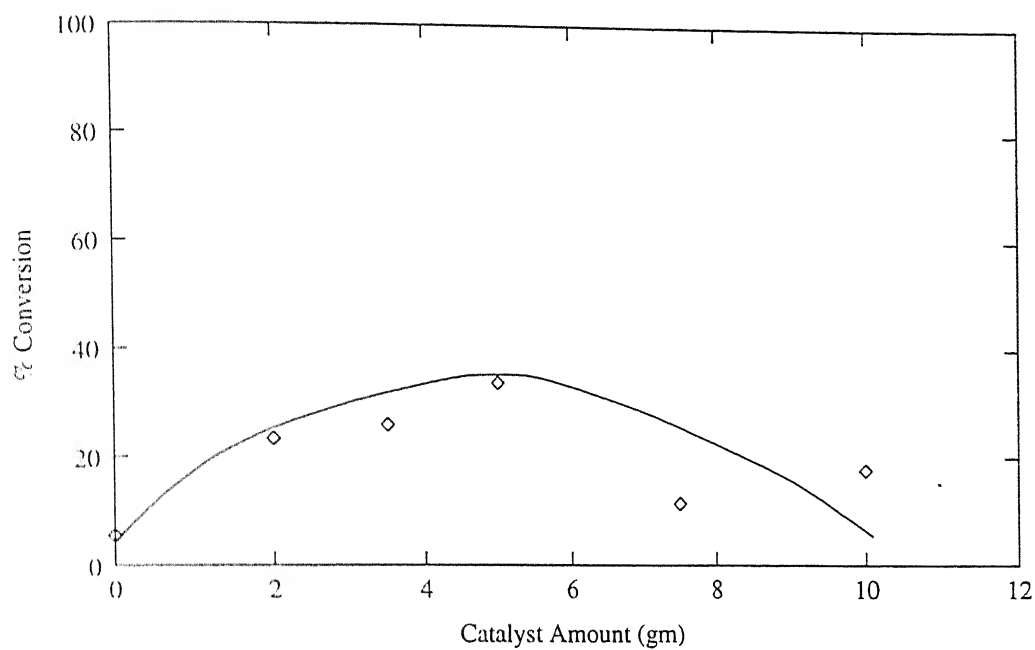


Figure 4.14: Effect of Amount of catalyst on % Conversion of n-hexane

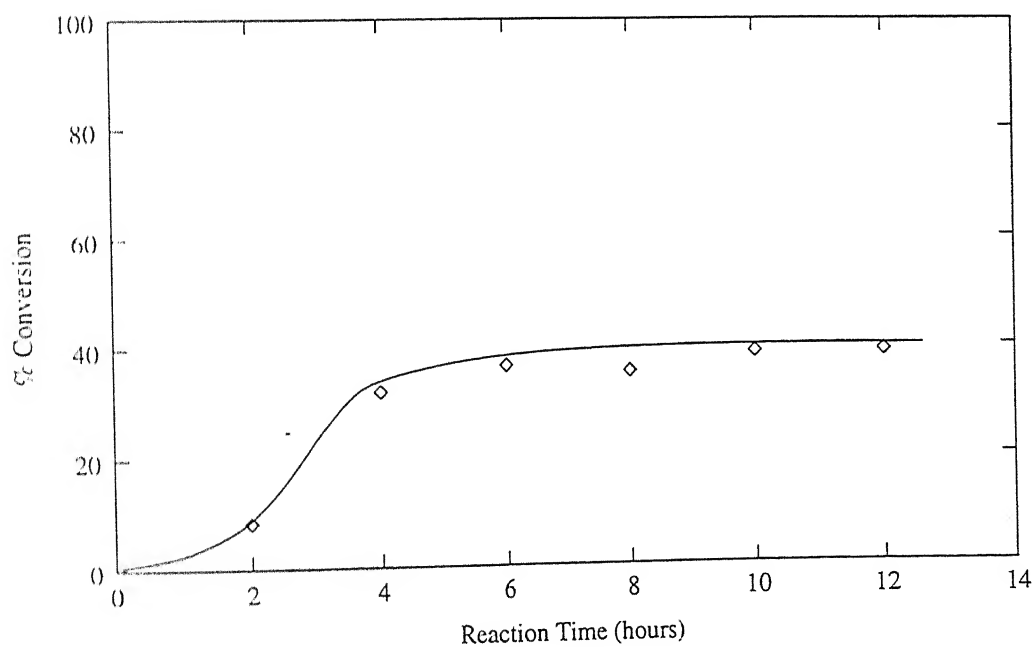


Figure 4.15: Effect of Reaction Time on % Conversion of n-hexane

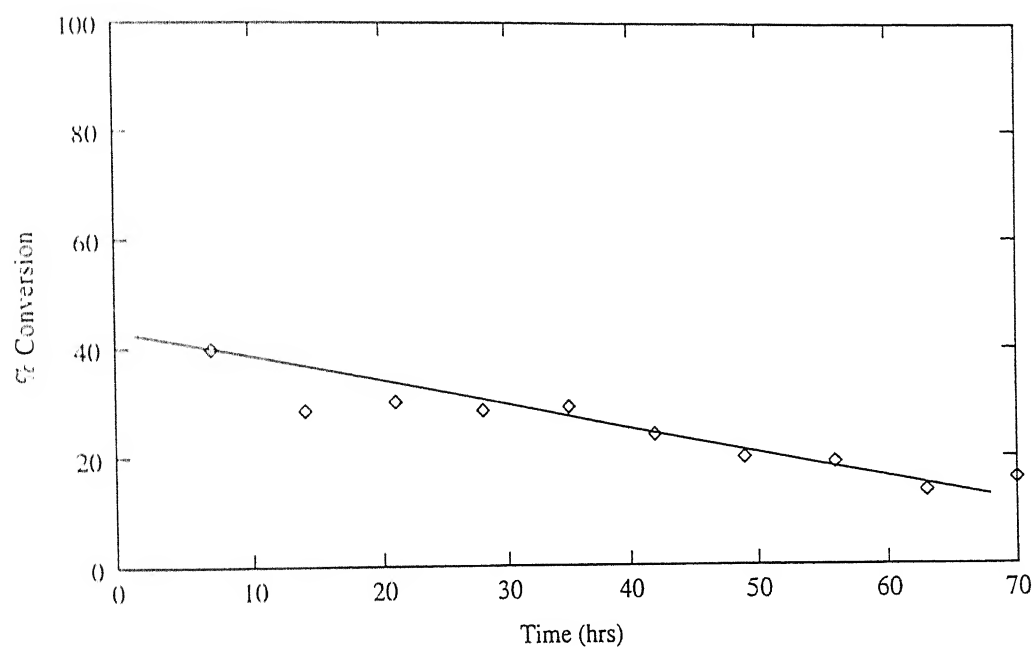


Figure 4.16: Effect of Recyclability of Catalyst on % Conversion of n-hexane

Chapter 5

Conclusions

In this thesis we have examined the effect of support on the heterogeneous catalysis in the oxidation of saturated hydrocarbons (n-hexane and paraffin wax). We have carried out the modifications of the polymer (styrene-divinylbenzene network) by attaching Salen Schiff base functional group sites on this beads and then chelated cobalt acetate. We have characterised these polymer beads for their particle size distribution and internal surface area. These supported catalysts are used for the oxidation of hydrocarbons like n-hexane and paraffin wax. We summarise our conclusions as follows.

- During the characterisation of the polymer beads it was observed that the gelatin content in the aqueous phase plays a vital role in controlling the average particle size of the beads and internal surface area of the particles. The average particle size was found to decrease and internal surface area was found to increase with the increase in gelatin content.
- The cobalt acetate catalyst was found to be highly selective towards the formation of alcohols at a very mild reaction conditions and no other product was determined to form during the reaction.
- The highest conversion of n-hexane was given by silicagel supported cobalt acetate.
- In the oxidation of n-hexane using silicagel supported catalyst it was observed that with increase in temperature the % conversion of n-hexane passes through a maxima suggesting a possible deactivation of catalyst at higher temperature.

- With increase in pressure the conversion also passes through a maxima. This result is attributed to the increased diffusional resistance to n-hexane offered due to blocking of pores at high pressure.
- With increase in amount of catalyst the conversion increases and reaches an asymptotic value at a catalyst amount of 5-6 g.
- With increase in the time the conversion increases reaching a steady state value after 8-9 hrs. This suggests that the oxidation reaction is an equilibrium reaction.
- Reuse of the catalyst for successive runs decreases the reaction to half of its initial value after 10 runs of 7 hours each (total 70 hours of use).
- The use of promotor was found to be essential for the oxidation reaction to occur.
- In the oxidation of paraffin wax we found out that at higher temperature and for the longer time of reaction the colourless product mixture turns light brown and the viscosity of the reaction mass decreases due to breakage of long hydrocarbon chains. The cobalt acetate supported on silicagel catalyst was found highly selective towards formation of alcohols.

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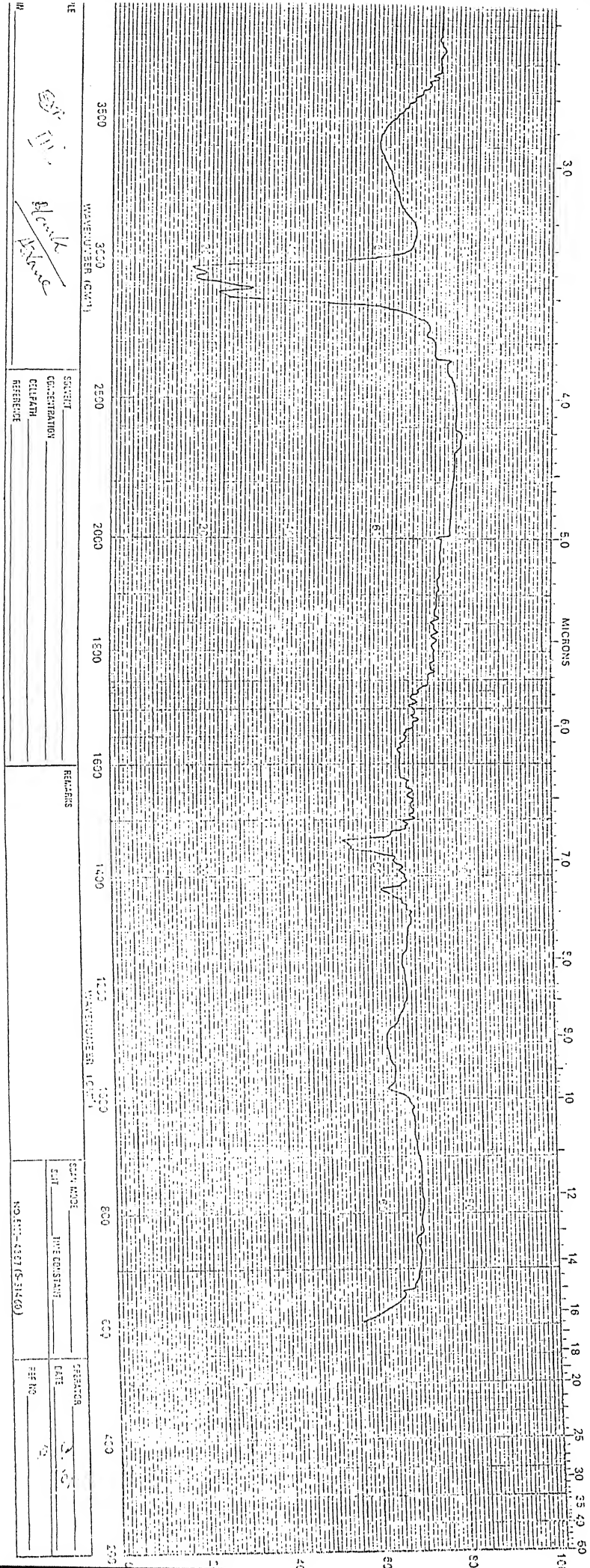
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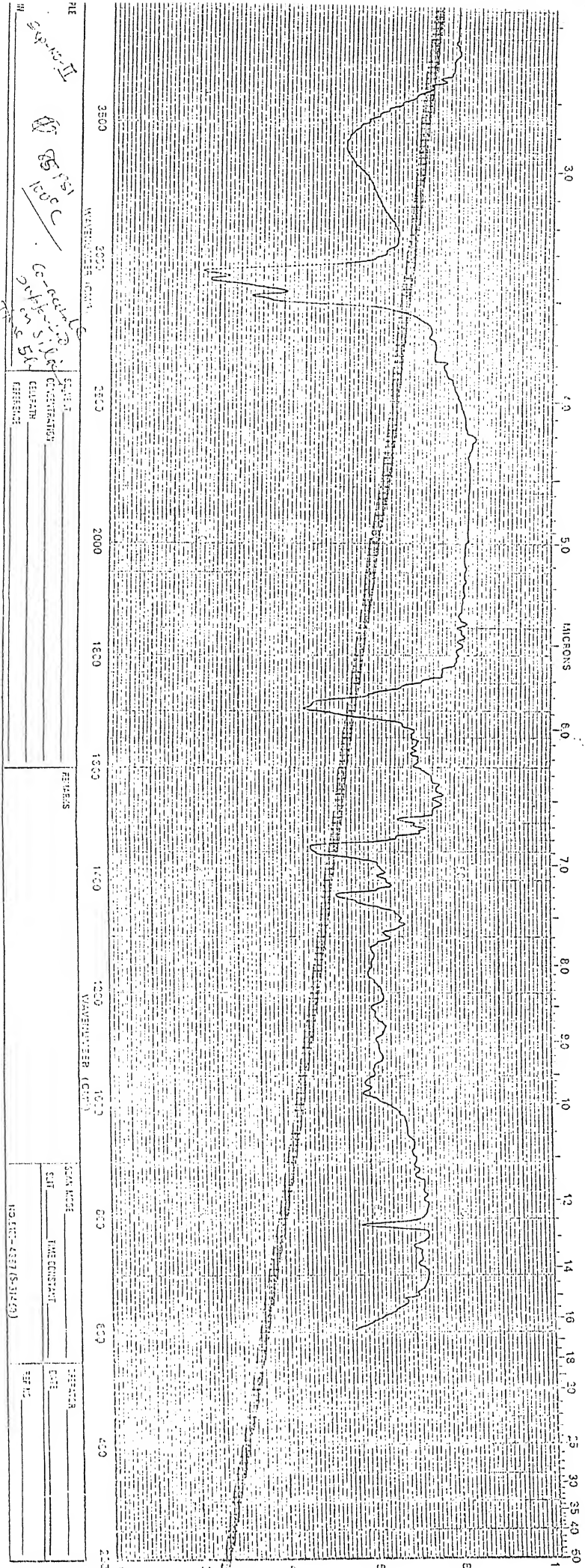
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Appendix I

The results obtained from IR spectroscopy of products and reactants (n-hexane) are attached herewith. The results obtained for elemental analysis of the catalyst from Electron Probe Micro Analyser are also attached herewith.





26-FEB-96 QUALITATIVE ANALYSIS

INTENSITY
(Counts)

File no. : 4
Comment : VAD SAL

1. 274 Acc. vol. 10.0 (kV) Smoothing Yes

2) CH-2 LIF MAX 1.
1) CH-1 NSTE 138. MIN 0.

Linear
Scale

0. 128.

-1.
SPECT.

-14.

5.000 mm

N

65.000 85.000 105.000 125.000 145.000 165.000

INTENSITY 29-FEB-96 QUALITATIVE ANALYSIS
(Counts) File no.: 1
Comment: TYROSCHIFF

1. 144. Acc. Vol. 10.0 (KV) Smoothing Yes

MAX MIN
1. 0.
69. 0.
2) CH-2 LIF
1) CH-1 NSTE

Linear
Scale

0. 68.

2) _____
1) _____

-1.
SPECT.

-8.

2.500 mm

(mm)

65.000

75.000

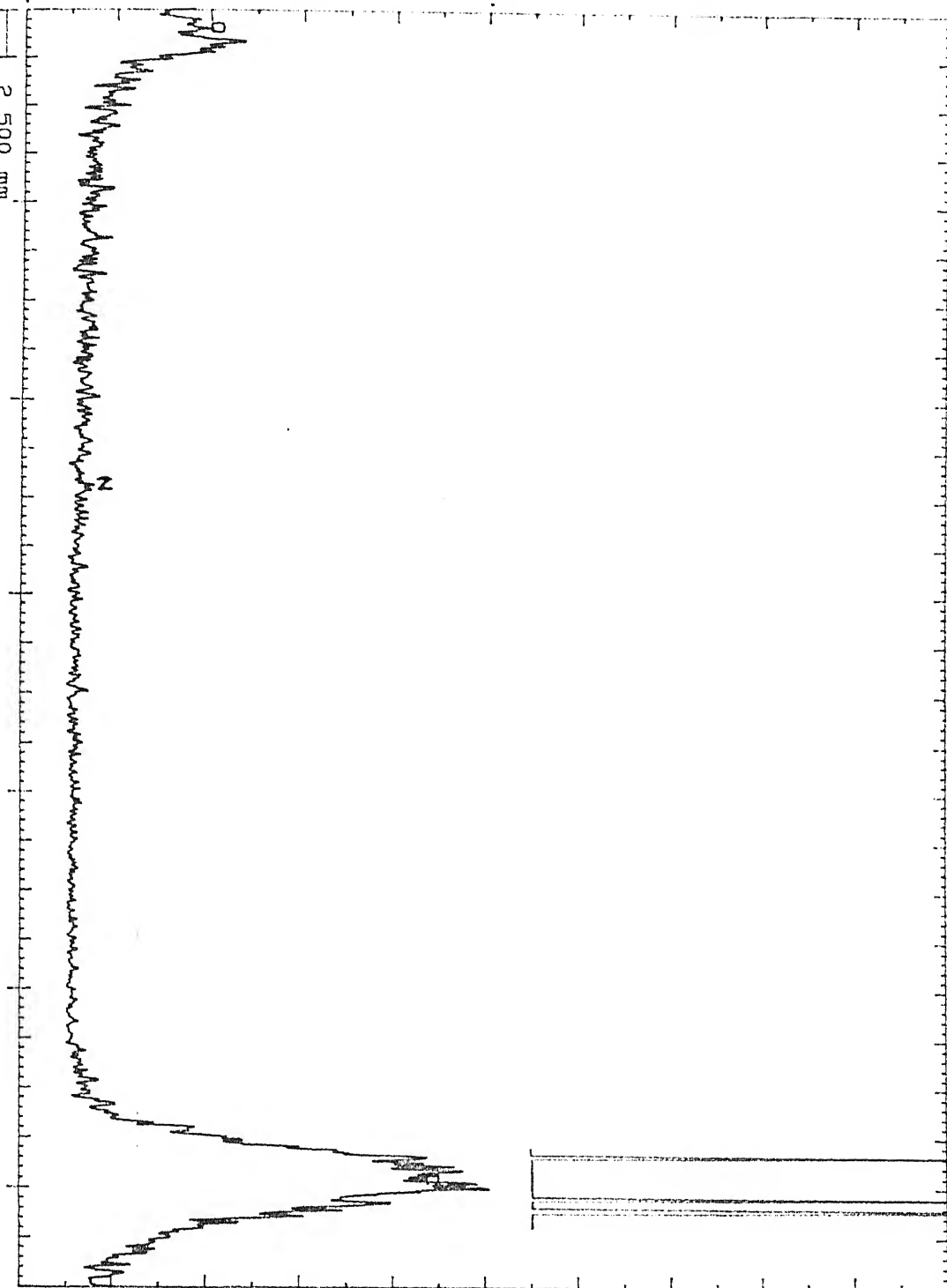
85.000

95.000

105.000

115.000

125.000



INTENSITY
29-FEB-96
QUALITATIVE ANALYSIS

File no. : 4
(Counts)
Comment : COSAL

1. 386. Acc. vol. 10.0 (kV) Smoothing yes

MAX MIN
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1) CH-1 NSTE 186. 0.

Linear
Scale

0. 183.

2) _____
1) _____

-2. SPECT.

(mm)

65.000

75.000

85.000

95.000

105.000

115.000

125.000

2.500 mm

-20.

